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I.

ON CERTAIN SUBSTITUTED CROTONOLACTONES AND MUCOBROMIC ACID.*

By Henry B. Hill and Robert W. Cornelison.

Presented April 12, 1893.

SEVERAL years ago a dichlorpyromucic acid was described by Hill and L. L. Jackson,† which differed from all the substituted pyromucic acids then known, in that it was readily decomposed by concentrated hydrochloric acid at 100° at ordinary pressures. Carbonic dioxide was evolved and a neutral body was formed which melted at 52–53°, and contained a percentage of chlorine which corresponded to the formula $C_4H_3ClO_2$. A body of similar properties melting at 77° had previously been found in small quantity by Hill and Sanger ‡ among the products formed from pyromucic tetrabromide by the action of an alcoholic solution of sodic hydrate. A complete analysis of this body had shown that its formula was $C_4H_3BrO_2$, but a lack of material ren-

---

* A part of the work described in the following paper was presented in the form of a thesis to the Faculty of Arts and Sciences of Harvard University in May, 1893, by Robert W. Cornelison, then candidate for the degree of Doctor of Philosophy.

† These Proceedings, XXIV. 348.   ‡ Ibid., XXI. 158.

dered a detailed study of it impossible. While the chlorine derivative
was more accessible, it was not more carefully studied by Hill and
L. L. Jackson since it was discovered only at the close of their inves-
tigation of the chlorpyromucic acids. They were also but partially
successful in determining the constitution of the χ-dichlorpyromucic
acid from which it was so easily formed. They showed that one
chlorine atom of this acid was in the δ position, but could bring for-
ward no definite facts to prove whether it was a βδ-dichlorpyromucic
acid stereometrically isomeric with the common form, or whether it
was the third possible structural isomer, the γδ-dichlorpyromucic acid.
In the former case its ready decomposition by aqueous hydrochloric
acid might be due to its peculiar configuration, in the latter case this
reaction might be conditioned by the simultaneous presence of halogens
in the γ and δ positions. If the instability of the acid were due to the
positions occupied by the halogen atoms, it seemed probable that the
tri-substituted pyromucic acids which also contain halogen in the γ and
δ places would show the same behavior. Although Hill and Sanger
had observed no such decomposition in studying tribrompyromucic
acid, and Hill and L. L. Jackson noticed no such reaction with the tri-
chlorpyromucic acid, in neither case had direct experiments in this
direction been made, and it was quite possible that the decomposition
in question had been overlooked. It was soon found, on trial, that tri-
brompyromucic acid was decomposed in analogous fashion, but that the
reaction was effected with much more difficulty, so that a temperature
materially above 100° was necessary in order to bring it about. When
heated to boiling with concentrated hydrobromic acid, carbonic dioxide
was evolved and a body melting at 90–91° was formed, which showed
a close resemblance to the monohalogenized bodies already known,
and which had the similar formula $C_4H_2Br_2O_2$. From trichlorpyro-
mucic acid the analogous body $C_4H_2Cl_2O_2$, melting at 50–51°, could
be made without difficulty. In studying the behavior of other substi-
tuted pyromucic acids under the same conditions, it was found that
the βδ-dibrompyromucic acid could also be made to undergo the same
decomposition, although but a comparatively small yield of a body
$C_4H_3BrO_2$ melting at 58° could thus be obtained. This mode of
decomposition was, therefore, not confined to those acids which con-
tained halogen at the same time in the γ and δ positions. By follow-
ing an entirely different method it was found that the βδ-dibrompyro-
mucic acid could be converted into an isomeric body, $C_4H_3BrO_2$, which
melted at 77°, and was identical with that which had already been
discovered by Hill and Sanger. The βδ-dibrompyromucic acid was

treated with bromine in aqueous solution, and the brommaleylbromide, $C_4HBr_3O_2$, which, according to the observations of Hill and Sanger,[*] is thus formed, when carefully reduced by zinc dust and glacial acetic acid, yielded the body melting at 77°. The mucobromylbromide $C_4HBr_3O_2$ described by Hill and O. R. Jackson[†] was so simply related, as far as its empirical formula was concerned, to the body $C_4H_2Br_2O_2$ formed from tribrompyromucic acid, that it seemed possible to establish experimentally a direct connection between the two. It was found that mucobromylbromide could readily be reduced by a variety of reducing agents, and that under certain conditions a nearly quantitative yield of the body $C_4H_2Br_2O_2$ melting at 90–91° could be obtained from it. Moreover, this reaction could be reversed and mucobromylbromide obtained by the action of bromine upon this reduction product. In the same way, by the reduction of mucochlorylbromide the body $C_4H_2Cl_2O_2$ melting at 50–51°, which had been made from trichlorpyromucic acid, could readily be obtained in any desired quantity.

Since the several bodies already mentioned were evidently perfectly similar in their structure, we chose for more detailed study the body $C_4H_2Br_2O_2$, which was the most readily accessible. The melting point of this substance, 90–91°, was not far removed from that assigned (88°) by Toennies[‡] to a body of like formula, which he obtained by the oxidation of $\beta\gamma$-dibrompyromucic acid with bromine water, and it was not difficult to suppose the two bodies identical. Toennies published no analyses whatsoever of his product, and Hill and Sanger[§] were unable to obtain the substance in larger quantities; but according to their observations a preparation which gave the proper percentage of bromine melted at 89–90°. A careful comparison of the substance prepared according to Toennies with that obtained by the decomposition of tribrompyromucic acid, or by the reduction of mucobromylbromide, showed the two bodies to be identical in every respect. The formation of dibrommaleic acid by the prolonged action of nitric acid upon this body sufficiently established the relative position of the two bromine atoms and left for its constitution the choice between the following formulæ : —
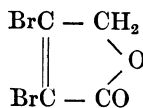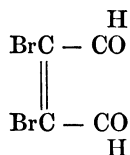
* These Proceedings, XXI. 166.

† Ibid., XVI. 174.

‡ Berichte d. deutsch. chem. Gesellsch., XII. 1202.

§ These Proceedings, XXI. 172.

$$\begin{array}{cc} \overset{\text{H}}{\underset{\text{H}}{\underset{\text{BrC}-\text{CO}}{\overset{\text{BrC}-\text{CO}}{\|}}}} & \underset{\text{BrC}-\text{CO}}{\overset{\text{BrC}-\text{CH}_2}{\|}} \diagup_{\diagdown} \text{O} \end{array}$$

Toennies found that his product could be converted into mucobromic acid by oxidation with chromic acid, and therefore considered it to be the double aldehyde of dibromfumaric acid. We found, on the other hand, that the body showed none of the ordinary characters of an aldehyde. On warming with chromic acid it was slowly oxidized, but mucobromic acid was not formed in quantity sufficient to enable us to identify it with precision. On long boiling with bromine and water mucobromic acid was formed. From concentrated nitric acid it could be recrystallized unchanged, and only after continued boiling was it oxidized to mucobromic and dibrommaleic acids. It did not combine with acid sodic sulphite, and did not react with hydroxylamine. Aniline in alcoholic solution removed one atom of bromine and gave a phenylamido derivative of the form $C_4H_2(C_6H_5NH)BrO_2$, and phenylhydrazine also removed bromine. Aqueous alkalies dissolved it with the formation of a deep yellow solution, but decomposition soon ensued with the elimination of hydrobromic acid. The whole behavior of the body was in direct opposition to the assumption that it was a double aldehyde, and the unsymmetrical structure was further established by the existence of two isomeric bodies of the same general constitution which contained a single bromine atom. The conclusion was inevitable that the body was a dibromcrotonolactone. The rigorous proof of its lactone structure, through its conversion into a salt of the corresponding oxy-acid was rendered difficult by the presence of the halogen since the halogen itself was rapidly removed in alkaline solution. By adding a decinormal solution of potassic hydrate to a cold dilute solution of the substance it is true that it was easy to prove that very nearly two molecules of potassic hydrate were neutralized in the reaction, while but one molecule of potassic bromide was formed, but it was impossible to isolate definite products of the decomposition. On reducing the body with zinc and dilute sulphuric acid the bromine was completely removed, and on distillation a feebly acid solution was obtained, which on titration with decinormal potassic hydrate proved to contain a lactone. By the usual methods an amorphous barium salt was obtained, which when thoroughly dried had the percentage composition required by a baric oxycrotonate. The isolation of the

crotonolactone itself proved to be a matter of such difficulty that we attempted to find some derivative which would be more manageable. The bodies containing the aniline residue in place of one of the halogen atoms were found to be useless for our purpose, since they were decomposed by boiling in alkaline solution with the formation of phenylisocyanide, and the phenylamidocrotonolactone formed from them by reduction was also decomposed with the formation of aniline under the same conditions. It seemed probable that the corresponding derivatives containing the phenoxy group would prove to be much more stable. While we have not yet succeeded in replacing the bromine of the body $C_4H_2Br_2O_2$ directly by the phenoxy group, we have had no difficulty in preparing such a body by the reduction of the bromanhydride of the mucophenoxybromic acid which was described by Hill and Stevens.* The body thus formed was easily shown to be a phenoxybromcrotonolactone, since it dissolved in hot alkaline solutions with the formation of the salts of the corresponding oxy-acid. On acidifying the well cooled akaline solution the phenoxybromoxycrotonic acid was obtained, which was stable under ordinary conditions, but which was again converted into the lactone by heat. These results were fully confirmed by a study of the phenoxychlorcrotonolactone, which was prepared by the reduction of mucophenoxychlorylbromide. The position which the phenoxy group takes in entering mucobromic acid has already been shown with sufficient precision by Hill and Stevens, since a remarkably stable phenoxybromacrylic acid is readily formed from this product by the action of alkalies. The phenoxylactones containing halogen must therefore have the constitution

$$
\begin{array}{cc}
BrC - CH_2 & ClC - CH_2 \\
\quad\; \| \quad\;\; \diagdown O & \quad\; \| \quad\;\; \diagdown O \\
\quad\quad\quad\; \diagup & \quad\quad\quad\; \diagup \\
C_6H_5OC - CO & C_6H_5OC - CO
\end{array}
$$

and the analogous bodies containing halogen alone the structure

$$
\begin{array}{cc}
BrC - CH_2 & ClC - CH_2 \\
\quad\; \| \quad\;\; \diagdown O & \quad\; \| \quad\;\; \diagdown O \\
\quad\quad\quad\; \diagup & \quad\quad\quad\; \diagup \\
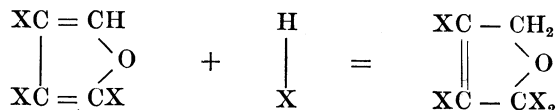BrC - CO & ClC - CO
\end{array}
$$

The formation of these bodies from tribrom- and trichlorpyromucic acids seems to us to be most readily explained by assuming that a trisubstituted furfuran is first formed with the loss of carbonic dioxide :

---

* These Proceedings, XIX. 262.

$$
\begin{array}{ccc}
\mathrm{XC = C - COOH} & & \mathrm{XC = CH} \\
\left| \quad {\searrow}\mathrm{O} \right. & = & \left| \quad {\searrow}\mathrm{O} \right. + \mathrm{CO_2} \\
\mathrm{XC = CX} & & \mathrm{XC = CX}
\end{array}
$$
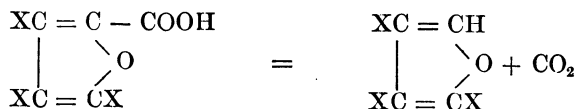
This then adds a molecule of haloid acid with the shifting of the double bond in a manner identical with that observed by v. Baeyer and Rupe * in the reduction of dichlormuconic acid:

$$
\begin{array}{ccccc}
\mathrm{XC = CH} & & \mathrm{H} & & \mathrm{XC - CH_2} \\
\left| \quad {\searrow}\mathrm{O} \right. & + & \left| \right. & = & \left\| \quad {\searrow}\mathrm{O} \right. \\
\mathrm{XC = CX} & & \mathrm{X} & & \mathrm{XC - CX_2}
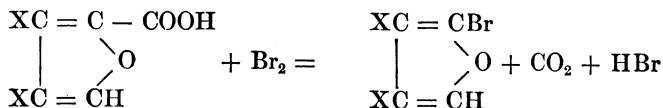\end{array}
$$

The addition product is then decomposed by water, giving the lactone. Possibly a molecule of water is directly added to the trisubstituted furfuran, giving

$$
\begin{array}{c}
\mathrm{XC - CH_2} \\
\left\| \quad {\searrow}\mathrm{O} \right. \\
\mathrm{XC - CX} \\
\qquad \mathrm{OH}
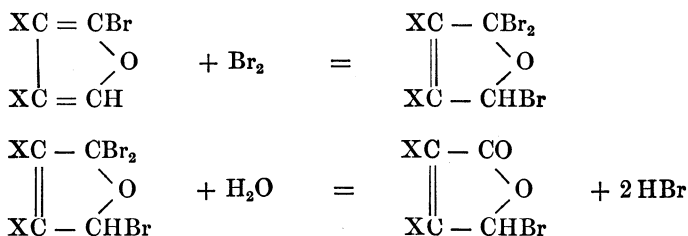\end{array}
$$
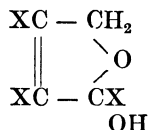
which would at once pass into the lactone by the loss of haloid acid.

The conversion of the βγ-dibrompyromucic acid into the dibromcrotonolactone, and of the βγ-dichlorpyromucic acid into the corresponding dichlorcrotonolactone by the action of bromine in aqueous solution likewise finds its explanation in the formation of a trisubstituted furfuran. In aqueous acid or alkaline solution the carboxyl of the substituted pyromucic acids is readily eliminated and replaced by bromine, as was first shown by Hill and Hartshorn † in the case of the δ-brompyromucic acid:

$$
\begin{array}{ccc}
\mathrm{XC = C - COOH} & & \mathrm{XC = CBr} \\
\left| \quad {\searrow}\mathrm{O} \right. \quad + \mathrm{Br_2} = & & \left| \quad {\searrow}\mathrm{O} \right. + \mathrm{CO_2} + \mathrm{HBr} \\
\mathrm{XC = CH} & & \mathrm{XC = CH}
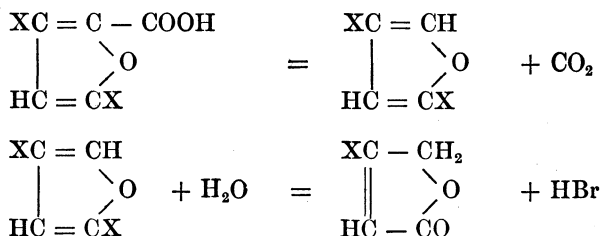\end{array}
$$

By the addition of water the substituted lactone is formed as before. We have shown that the bromanhydrides of mucobromic and mucochloric acids are also formed in this same reaction. This formation is evidently due to the addition of bromine to the trisubstituted furfuran and the decomposition of this product by water:
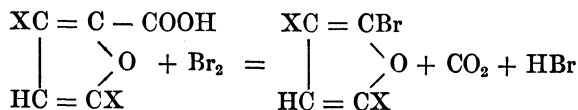
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* Ann. Chem. u. Pharm., CCLVI. 25.

† Berichte d. deutsch. chem. Gesellsch., XVIII. 448.

$$
\begin{array}{cc}
\begin{array}{c} XC = CBr \\ \Big| \quad \diagdown O \\ XC = CH \diagup \end{array} + Br_2 & = &
\begin{array}{c} XC - CBr_2 \\ \| \quad \diagdown O \\ XC - CHBr \diagup \end{array}
\end{array}
$$

$$
\begin{array}{cc}
\begin{array}{c} XC - CBr_2 \\ \| \quad \diagdown O \\ XC - CHBr \diagup \end{array} + H_2O & = &
\begin{array}{c} XC - CO \\ \| \quad \diagdown O \\ XC - CHBr \diagup \end{array} + 2\,HBr
\end{array}
$$

It has already been said that two isomeric monosubstituted crotono-lactones may be made by appropriate means from the disubstituted pyromucic acids containing the halogens in the β and δ positions. By heating these substituted pyromucic acids with mineral acids the brom- and chlorcrotonolactones melting at 58° and 26° respectively may be made. The reaction is evidently perfectly analogous to the decomposition of the trisubstituted pyromucic acids under like conditions which has just been discussed. The carboxyl group is replaced by hydrogen with the loss of carbonic dioxide and the substituted furfuran thus formed then passes into the lactone as before:
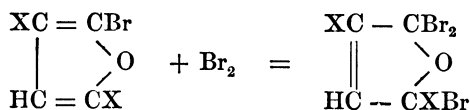
$$
\begin{array}{cc}
\begin{array}{c} XC = C - COOH \\ \Big| \quad \diagdown O \\ HC = CX \diagup \end{array} & = &
\begin{array}{c} XC = CH \\ \Big| \quad \diagdown O \\ HC = CX \diagup \end{array} + CO_2
\end{array}
$$

$$
\begin{array}{cc}
\begin{array}{c} XC = CH \\ \Big| \quad \diagdown O \\ HC = CX \diagup \end{array} + H_2O & = &
\begin{array}{c} XC - CH_2 \\ \| \quad \diagdown O \\ HC - CO \diagup \end{array} + HBr
\end{array}
$$

The β-substituted lactones which are thus formed may be made much more conveniently by the partial reduction of the disubstituted lactones. In order to prepare the monohalogenized crotonolactones with the halogen in the α position from the $\beta\delta$-dichlor- and dibrompyromucic acids, derivatives of maleic acid must first be formed. The first step in the reaction is the formation of a trisubstituted furfuran through the replacement of the carboxyl by bromine:
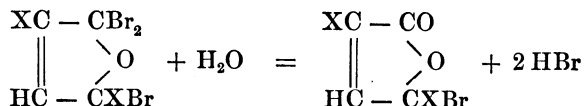
$$
\begin{array}{cc}
\begin{array}{c} XC = C - COOH \\ \Big| \quad \diagdown O \\ HC = CX \diagup \end{array} + Br_2 & = &
\begin{array}{c} XC = CBr \\ \Big| \quad \diagdown O \\ HC = CX \diagup \end{array} + CO_2 + HBr
\end{array}
$$

Through the addition of bromine with the shift of the double bond, as before,

$$
\begin{array}{c}
XC = CBr \\
\Big| \qquad \diagdown O \\
\qquad \diagup \\
HC = CX
\end{array}
\; + Br_2 \; = \;
\begin{array}{c}
XC - CBr_2 \\
\| \qquad \diagdown O \\
\qquad \diagup \\
HC -\!\!- CXBr
\end{array}
$$

a body is formed which through the action of water yields the derivative of maleic acid:

$$
\begin{array}{c}
XC - CBr_2 \\
\| \qquad \diagdown O \\
\qquad \diagup \\
HC - CXBr
\end{array}
\; + H_2O \; = \;
\begin{array}{c}
XC - CO \\
\| \qquad \diagdown O \\
\qquad \diagup \\
HC - CXBr
\end{array}
\; + 2\,HBr
$$

This in its turn gives the lactone by reduction:

$$
\begin{array}{c}
XC - CO \\
\| \qquad \diagdown O \\
\qquad \diagup \\
HC - CH_2
\end{array}
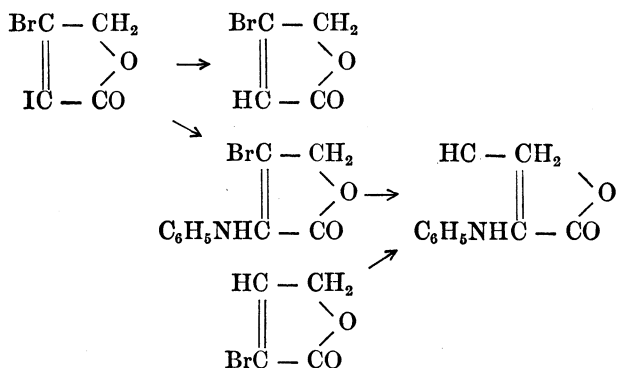$$
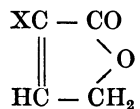
In the case of the $\beta\delta$-dibrompyromucic acid the tribromfurfuran, which should appear as the intermediate product in this reaction, has been isolated in a pure condition by Mr. W. M. Booth in this Laboratory, and been found to yield, when treated with bromine in aqueous solution, the brommaleylbromide described by Hill and Sanger.

The a-bromcrotonolactone may also be formed by the action of bromine in aqueous solution upon β-brompyromucic acid. The reaction is evidently identical with that through which the dibromcrotonolactone is formed from $\beta\gamma$-dibrompyromucic acid. A dibromfurfuran is first formed, which by the fixation of water and the elimination of hydrobromic acid passes into the lactone:

$$
\begin{array}{c}
BrC = C - COOH \\
\Big| \qquad \diagdown O \\
\qquad \diagup \\
HC = CH
\end{array}
\; + Br_2 \; = \;
\begin{array}{c}
BrC = CBr \\
\Big| \qquad \diagdown O \\
\qquad \diagup \\
HC = CH
\end{array}
\; + CO_2 + HBr
$$

$$
\begin{array}{c}
BrC = CBr \\
\Big| \qquad \diagdown O \\
\qquad \diagup \\
HC = CH
\end{array}
\; + H_2O \; = \;
\begin{array}{c}
BrC - CO \\
\| \qquad \diagdown O \\
\qquad \diagup \\
HC - CH_2
\end{array}
\; + HBr
$$
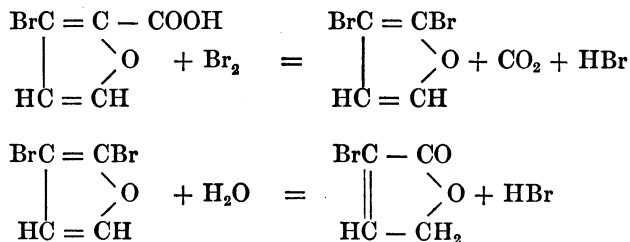
The isomerism observed in the monohalogenized crotonolactones must be due to the position of the halogen atoms, since, according to the views at present held concerning geometric isomerism, lactones can be formed from the maleinoid forms only. A definite proof that the
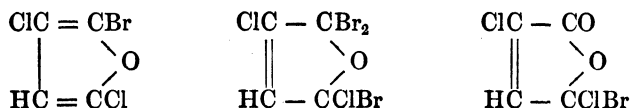
halogen atoms in the a- and β-bromcrotonolactones are attached to different carbon atoms is easily given. The $a\beta$-dibromcrotonolactone yields with hydriodic acid an iodine derivative which can be reduced to β-bromcrotonolactone. This same iodine compound gives with aniline a phenylamidobromcrotonolactone which on reduction is converted into the same phenylamidocrotonolactone that may be made by the action of aniline upon the a-bromcrotonolactone :

$$\underset{\underset{\displaystyle I\overset{|}{C} - CO}{}}{BrC - CH_2} \diagdown O \quad \rightarrow \quad \underset{\underset{\displaystyle H\overset{|}{C} - CO}{}}{BrC - CH_2} \diagdown O$$

$$\underset{\underset{\displaystyle C_6H_5NH\overset{|}{C} - CO}{}}{BrC - CH_2} \diagdown O \rightarrow \underset{\underset{\displaystyle C_6H_5NH\overset{|}{C} - CO}{}}{HC - CH_2} \diagdown O$$

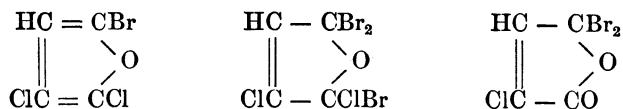$$\underset{\underset{\displaystyle Br\overset{|}{C} - CO}{}}{HC - CH_2} \diagdown O$$

It is evident that the acid described by Hill and L. L. Jackson under the provisional name of the χ-dichlorpyromucic acid, since it readily gives the a-chlorcrotonolactone on decomposition with mineral acids, must in fact be the $\gamma\delta$-dichlorpyromucic acid, and its structure

$$\underset{\underset{\displaystyle Cl\overset{|}{C} = CCl}{}}{HC = C - COOH} \diagdown O$$
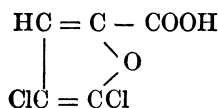
It is perhaps worthy of note that, although the $\beta\delta$- and the $\gamma\delta$-dichlorpyromucic acids give the two isomeric chlorcrotonolactones when heated with acids, they give the same a-chlorcrotonolactone when they are treated with bromine in aqueous solution, and the resulting product it reduced. Evidently two isomeric dichlorbromfurfurans are first formed, which yield the corresponding addition products with bromine, but these addition products are attacked by water in such a way that in each case the chlorine is left in the a position with regard to the oxidized carbon :

$$\underset{\underset{\displaystyle H\overset{|}{C} = CCl}{}}{ClC = CBr} \diagdown O \qquad \underset{\underset{\displaystyle H\overset{|}{C} - CClBr}{}}{ClC - CBr_2} \diagdown O \qquad \underset{\underset{\displaystyle H\overset{|}{C} - CClBr}{}}{ClC - CO} \diagdown O$$

$$
\begin{array}{ccc}
\mathrm{HC} = \mathrm{CBr} & \mathrm{HC} - \mathrm{CBr_2} & \mathrm{HC} - \mathrm{CBr_2} \\
\parallel \qquad \searrow \mathrm{O} & \parallel \qquad \searrow \mathrm{O} & \parallel \qquad \searrow \mathrm{O} \\
\mathrm{ClC} = \mathrm{CCl} & \mathrm{ClC} - \mathrm{CClBr} & \mathrm{ClC} - \mathrm{CO}
\end{array}
$$

The close relationship between mucobromic acid and bodies which have thus been shown to be derivatives of crotonolactone naturally recalled the suggestions which had already been made as to the constitution of mucobromic acid itself. As early as 1882 Roser [*] pointed out that the so called fumaric aldehyde acid of Limpricht might in reality be an oxylactone,

$$
\begin{array}{c}
\qquad\qquad \mathrm{H} \\
\mathrm{HC} - \mathrm{COH} \\
\parallel \qquad \searrow \mathrm{O} \\
\mathrm{HC} - \mathrm{CO}
\end{array}
$$
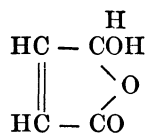
and afterward in 1887 Anschütz,[†] in his interesting and suggestive discussion of the constitution of maleic and fumaric acids, was led to the conclusion that mucobromic acid was an oxydibromcrotono-lactone :

$$
\begin{array}{c}
\qquad\qquad \mathrm{H} \\
\mathrm{BrC} - \mathrm{COH} \\
\parallel \qquad \searrow \mathrm{O} \\
\mathrm{BrC} - \mathrm{CO}
\end{array}
$$
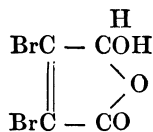
It was evident that the almost quantitative reduction of mucobromyl-bromide by such a reducing agent as stannous chloride in the cold was perfectly intelligible if the formula of this bromide were

$$
\begin{array}{c}
\qquad\qquad \mathrm{H} \\
\mathrm{BrC} - \mathrm{CBr} \\
\parallel \qquad \searrow \mathrm{O} \\
\mathrm{BrC} - \mathrm{CO}
\end{array}
$$
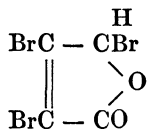
while the formation of a lactone under these conditions from the bromanhydride derived from the aldehyde acid

$$
\begin{array}{c}
\mathrm{BrC} - \mathrm{C}{<}^{\mathrm{H}}_{\mathrm{O}} \\
\parallel \\
\mathrm{BrC} - \mathrm{COBr}
\end{array}
$$

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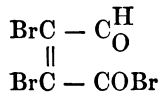
[*] Berichte d. deutsch. chem. Gesellsch., XV. 1523.

[†] Ann. Chem. u. Pharm., CCXXXIX. 161.

could hardly be explained except by assuming that the aldehyde group was itself first attacked, and the lactone then formed by the elimination of hydrobromic acid from the body

$$\begin{array}{l} \text{BrC} - \text{C}^{\text{H}_2}_{\text{OH}} \\ \quad \| \\ \text{BrC} - \text{COBr} \end{array}$$
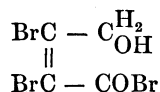
This explanation seemed to us exceedingly improbable, and we furthermore showed by direct experiment that no perceptible amount of the dibromcrotonolactone could be formed by the action of stannous chloride and hydrochloric acid upon mucobromic acid itself, or by its reduction with zinc and acetic acid, while the alcohol acid

$$\begin{array}{l} \text{BrC} - \text{C}^{\text{H}_2}_{\text{OH}} \\ \quad \| \\ \text{BrC} - \text{COOH} \end{array}$$
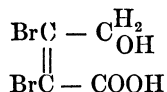
which would be formed if the aldehyde group were readily reduced would certainly yield the lactone with facility. The ready formation of mucobromylbromide by the action of bromine at 100° upon the dibromcrotonolactone seemed equally conclusive, and the lactone formula for mucobromylbromide established. Since phosphorous tribromide converts mucobromic acid almost quantitatively into its bromanhydride, the lactone structure of mucobromic acid itself seemed to be proved. It can hardly be supposed that a bromide of the lactone formula could be formed from the aldehyde acid, for this would imply the replacement of the aldehyde oxygen through the phosphorous tribromide leaving the hydroxyl of the carboxyl group to form the lactone by the elimination of hydrobromic acid. Although Hill and O. R. Jackson * showed many years ago that mucobromic acid could readily be converted into dibrommaleic acid by means of argentic oxide, it was evident that even this mode of oxidation no longer warranted a definite conclusion as to its aldehyde character. We therefore thought it necessary to take up the study of the behavior of mucobromic and mucochloric acids, as well as the related acids containing the phenoxy group, toward hydroxylamine. We found that these four acids gave oximes with ease, and in studying more in detail the compounds formed from mucobromic acid we found that they were perfectly analogous to the bodies formed by the action of hydroxylamine upon opianic, phthalaldehydic, and pseudopianic acids as

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* These Proceedings, XVI. 186.

described by Lieberman,[*] Allendorf,[†] Racine,[‡] and Perkin.[§]   Muco-
bromoxime is so unstable that it passes spontaneously into its anhy-
dride, and can be formed only by the action of free hydroxylamine in
aqueous solution.   The anhydride is formed through the hydrochlorate
in alcoholic solution, and by boiling this alcoholic solution or by heat
alone is converted into dibrommaleinimide.   The oxime or its anhy-
dride is further converted into the acid ammonium salt of dibrom-
maleic acid by boiling it with water.   The ready formation of oximes
of perfectly normal character from mucobromic acid would in itself
naturally be considered as establishing the aldehyde character of this
acid.   Still the difficulty in explaining the conversion of the broman-
hydride of an aldehyde acid into a lactone by reduction with stannous
chloride in the cold is so great that it seems to us more rational to
suppose either that hydroxylamine acts directly upon an oxylactone of
this type and that the ordinary oxime is then formed by molecular
rearrangement, or that under the conditions of the reaction the hydrox-
ylamine acts only through the fixation of a molecule of water, and the
breaking of the lactone ring with formation of the aldehyde acid.

In this connection we were interested to know whether the esters
of mucobromic acid would enter into reaction as readily as the free
acid.   While it seemed probable that the ester of the aldehyde acid
of the form

$$BrC - C^H_O$$
$$\|$$
$$BrC - COOCH_3$$
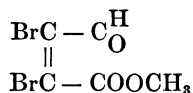
would be attacked by hydroxylamine quite as readily as the free acid,
the ester formed from the oxylactone.

$$BrC - C - OCH_3$$
$$\| \qquad \searrow O$$
$$BrC - CO \nearrow$$
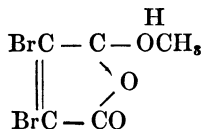
might well prove more refractory.   Several years ago Lieberman[||]
tried the behavior of the ethylester of opianic acid with hydroxylamine,

* Berichte d. deutsch. chem. Gesellsch., XIX. 2278, 2923.
† Ibid., XXIV. 3264.
‡ Ann. d. Chem. u. Pharm., CCXXXIX. 81.
§ Journ. Chem. Soc., LVII. 1069.
|| Berichte d. deutsch. chem. Gesellsch., XIX. 2926.

and obtained only the opianic oxime anhydride. We have been able
to find described no other experiments with the esters of the acids
in question. Our own experiments with mucobromic acid, and its
methyl ester, showed that the ester was attacked with much more
difficulty. While mucobromic acid is rapidly converted into its oxime
and oxime anhydride, we failed to discover any appreciable action
when hydroxylamine is added to a solution of methyl mucobromate in
methyl alcohol at ordinary temperatures even after the lapse of several
days. On boiling, the methyl ester of mucobromoxime was formed,
identical with the body formed by heating mucobromoxime with methyl
alcohol. Further experiments in this direction can alone show whether
the difference in behavior between the acids of this series and their
esters is sufficiently general to warrant definite conclusions as to their
structure. The action of phenylhydrazine upon mucobromic and
mucochloric acids and their esters, which we hoped to study in detail,
proved to yield bodies which were not suitable for investigation.

Many years ago Mr. C. W. Andrews, who was at that time an
assistant in this Laboratory, made some experiments as to the action
of aniline upon mucobromic acid and its ethyl ester, which he was
unable to complete at the time, and which have never been published.
He found that the reaction with mucobromic acid was complex, in that
bromine was partially replaced by the aniline residue, and also that
oxygen was eliminated by condensation. In marked contrast with
this reaction was the behavior of ethyl mucobromate with aniline.
One atom of bromine was here replaced, but the rest of the molecule
remained unaltered, so that the body $C_4H_2Br(NHC_6H_5)O_3C_2H_5$
was formed in nearly theoretical quantity. It therefore seemed to us
of interest to determine whether ethyl mucobromate would behave
in an analogous way with ammonia. We found, however, in this
case, that the reaction took a different course, and that the ethoxy
group was first attacked. The body which is thus formed has the
formula of the amide of mucobromic acid, but its behavior is in some
respects anomalous. It dissolves readily in caustic alkalies, and may
be reprecipitated unchanged by immediate acidification. It is but
slowly converted into mucobromic acid by boiling with mineral acids,
and with oxidizing agents it yields dibrommaleinimide. From muco-
chloric acid a body of similar properties was obtained.

$\alpha\beta$-DIBROMCROTONOLACTONE.

Although tribrompyromucic acid is little affected by boiling hydro-
chloric acid, it is quite readily decomposed, with the escape of carbonic

dioxide, when heated to 130° with diluted sulphuric acid (sp. gr. 1.43), or when boiled with concentrated hydrobromic acid. The reaction seemed to be more neatly effected with the latter reagent, and we therefore heated tribrompyromucic acid with from four to five times its weight of concentrated hydrobromic acid with a return condenser. When no further escape of carbonic dioxide could be detected, the somewhat dark colored clear solution was cooled, and diluted with water. A heavy crystalline precipitate was thus thrown down, which could easily be purified by recrystallization from alcohol or ligroin. The crude product obtained in this way amounted to about half the weight of the tribrompyromucic acid taken. Analyses of the body after several recrystallizations from alcohol showed that it had the formula $C_4H_2Br_2O_2$. For the analyses of this dibromcrotonolactone, and of several of its derivatives, which we publish, we are indebted to Mr. H. N. Herman, who made a preliminary study of this body seme two years ago, but was unable to continue the investigation.

I.   0.2472 grm. substance gave 0.1788 grm. CO_2 and 0.0209 grm. H_2O.
II. 0.2394 grm. substance gave 0.3711 grm. AgBr.

	Calculated for $C_4H_2Br_2O_2$.	Found.	
		I.	II.
C	19.83	19.73	
H	0.83	0.94	
Br	66.12		65.96

This same body may also be made directly from mucobromic acid by the action of phosphorous iodide. Phosphorus is dissolved in five times its weight of carbonic disulphide, equivalent weights of iodine and mucobromic acid well ground together are then added, and the nearly solid mass heated on the water bath with reverse cooler. The reaction sets in slowly, and frequently only after a part of the carbonic disulphide has been allowed to escape through the cooler. With no solvent present the reaction is violent and yields little or no product. When the mass is completely liquefied, the rest of the carbonic disulphide is distilled off, the flask well cooled, and cold water added in not too small quantity. On shaking, the crude lactone separates in a granular condition. In this way it is easy to obtain a product which amounts to two thirds of the weight of the mucobromic acid taken, but it contains a decided percentage of iodine, and the preparation of pure dibromcrotonolactone from it is a matter of great difficulty. By fractional crystallization from various solvents we found it impossible to eliminate the iodine, but on distillation with

steam the substance first carried over contained but little, and the percentage of iodine did not become large until about one half of the material taken had passed over. The material which had thus been partially purified by fractional distillation with steam, could not be further purified by recrystallization, but after boiling for some time with bromine water the iodine compound was oxidized, and a substance was then obtained which after several recrystallizations from alcohol possessed the properties and the composition of pure dibromcrotonolactone.

<div align="center">0.2439 grm. substance gave 0.3779 grm. Ag Br.</div>

	Calculated for $C_4H_2Br_2O_2$.	Found.
Brm.	66.12	65. 93

The dibromcrotonolactone can much more readily be made from mucobromic acid by the reduction of its bromanhydride. Muco-bromylbromide was described many years ago by Hill and O. R. Jackson,[*] who made it by the action of phosphoric pentabromide upon mucobromic acid. We have found that phosphorous tribromide is in many respects more advantageous for its preparation. The reaction runs somewhat slowly at 100°, but so smoothly that one molecule of the tribromide is sufficient for three molecules of mucobromic acid, and the yield is about 90 per cent of the theoretical amount. After the reaction is over the flask is well cooled, cold water is added, and the whole vigorously shaken until the oil which first separates solidifies in a granular form. The crude product melts at 54–55°, and by repeated recrystallization from small quantities of hot alcohol this melting point may be raised to 56–57°, one degree higher than the point given by Hill and O. R. Jackson. We attempted to purify the crude product by distillation in vacuo, but we found that the melting point was depressed rather than raised by this treatment. We have not further studied the change which is thus apparently brought about by distillation, for we soon found that a perfectly pure dibromcrotono-lactone could be made directly from the mucobromylbromide, as it was precipitated by water, while it was difficult, if not impossible, to do this with the distilled substance of low melting point. Hydriodic acid, or zinc dust with glacial acetic acid, reduces the mucobromyl-bromide to the lactone, although the former reagent yields a product which contains iodine. A far more efficient and convenient reducing

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[*] These Proceedings, XVI. 174.

agent we found to be stannous chloride with hydrochloric acid, since this gives at once an essentially pure product in satisfactory quantity. Mucobromylbromide is added to an equal weight of stannous chloride dissolved in the same amount of concentrated hydrochloric acid. The reduction proceeds rapidly with the evolution of heat, although in working with small quantities the reaction is greatly facilitated by warming gently at first. When the melting point of the mucobromylbromide is reached, the flask must be well shaken until the oil has completely disappeared. As the solution cools the dibromcrotonolactone crystallizes out, and still more separates on dilution. The yield which may be obtained in this way amounts to from 75 to 80 per cent of the weight calculated from the mucobromylbromide taken, or about 70 per cent of that theoretically required by the mucobromic acid employed. A single recrystallization from alcohol is sufficient for its complete purification.

Dibromcrotonolactone is very sparingly soluble in cold water, and dissolves in from 30 to 40 times its weight of boiling water. As the hot aqueous solution cools, the lactone crystallizes in small six-sided plates, or in pointed prisms crossing at an angle of 60°. From alcohol, in which it is somewhat sparingly soluble at ordinary temperatures, although very readily soluble on heating, it crystallizes in bundles of long friable prisms. From concentrated nitric acid it crystallizes in large, clear, brilliant oblique prisms. In boiling ligroin it dissolves somewhat sparingly on boiling, and as the solution cools the greater part of it separates in finely felted needles. It is readily soluble in chloroform or benzol, more sparingly soluble in ether or carbonic bisulphide. It melts at 90–91°, and boils under a pressure of 18 mm. at 145°. With steam it volatilizes rapidly. Although it is remarkably stable in acid solutions, it is easily attacked by alkalies. The alkaline hydrates dissolve it, forming deep yellow solutions, and at the same time alkaline bromides are formed. In studying the action of decinormal potassic hydrate in the cold, we have found that approximately two molecules of potassic hydrate are neutralized by each molecule of the lactone taken, while but one molecule of potassic bromide is formed, but have been able to isolate no definite products of the reaction. The lactone was not attacked by hydroxylamine; with aniline it yielded, with the elimination of bromine, the well crystallized aniline derivative, which will be described later. Phenylhydrazine also removed bromine, but gave no well characterized product.

Dibromfumaric Aldehyde of Toennies.

The melting point and other properties of the dibromcrotonolactone recalled a body of like composition which was obtained in 1879 by Toennies,* through the action of bromine water upon $\beta\gamma$-dibrompyro-mucic acid. He gives no analytical data to support his formula, and apparently had but small quantities of material at his disposal. From its behavior he considered the body to be the aldehyde of mucobromic acid, or the double aldehyde of dibromfumaric acid. In 1866 Hill and Sanger † again prepared this body from $\beta\gamma$-dibrompyromucic acid, but were unable to obtain it in satisfactory quantities, and hoped to return to it at some future time. A further study of the reaction has shown us that it is by no means simple in its nature. While we have been unable to obtain a satisfactory yield of the desired product, we have succeeded in preparing an amount amply sufficient for its identification, and at the same time we have isolated a second product of the reaction.

Preliminary experiments showed us that it was most advantageous to add about 20 per cent more than one molecule of bromine to the finely divided dibrompyromucic acid suspended in 20 times its weight of cold water. We therefore boiled 5 grm. of pure $\beta\gamma$-dibrompyro-mucic acid with 100 c.c. of water, and quickly cooled the solution in order to obtain the acid in a finely divided condition. When the temperature reached 16°, 1.2 c.c. of bromine were added, and the whole well shaken. The color of the bromine gradually faded, but when it had completely disappeared a considerable amount of a well crystallized body remained undissolved. Instead of allowing the solution to stand over night, as Hill and Sanger had done, we filtered out the insoluble substance at the end of three hours, and extracted the colorless aqueous solution thoroughly with ether. The ethereal extract left on distillation a syrupy residue, which partially solidified on standing over night *in vacuo* over sulphuric acid. The crystals when thoroughly drained upon the pump and pressed weighed 0.85 grm. Two crystallizations from small quantities of hot alcohol yielded 0.65 grm. of substance, which melted at 90–91°, and showed the characteristic behavior of the dibromcrotonolactone. In order to identify it with precision, we converted it into the a-iod-β-bromcroto-nolactone, which is fully described later, by heating it with hydriodic

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* Berichte d. deutsch. chem. Gesellsch., XII. 1202.
† These Proceedings, XXI. 172.

acid, and found the product to melt at the proper point, 118–119°. On reduction with zinc and acetic acid it yielded the β-bromcrotono-lactone melting at 57–58°, and with aniline the α-phenylamido-β-bromcrotonolactone with its characteristic properties, both of which bodies, as we shall afterwards show, may be made in the same way from the dibromcrotonolactone. As we shall show more fully later, we were unable to confirm the statement of Toennies that the dibrom-crotonolactone could easily be converted into mucobromic acid by oxidation with chromic acid. By the action of bromine in aqueous solution a part of the βγ-dibrompyromucic acid had been converted into dibromcrotonolactone, according to the equation given by Toennies,

$$C_5H_4Br_2O_3 + Br_2 + H_2O = C_4H_2Br_2O_2 + CO_2 + 2\,HBr.$$
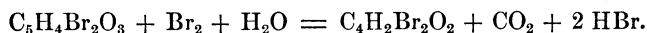
The viscous oil which had been drained from the crystalline product deposited a few more crystals of the lactone on long standing, but we have not yet examined it further. The insoluble matter, which had been removed by filtration before the extraction with ether, was washed with a dilute solution of sodic carbonate. But a small amount dissolved, and upon acidification 0.2 grm. of a sparingly soluble acid was precipitated, which melted at 189–190°, and was evidently unaltered dibrompyromucic acid. The residue, insoluble in the alkaline solution, weighed 1 grm., and consisted chiefly of mucobromylbromide. It gave in alcoholic solution a deep blue evanescent color on the addition of sodic carbonate, and one crystallization from alcohol was sufficient to raise the melting point to 56–57°. A part of the di-brompyromucic acid had therefore been decomposed according to the equation

$$C_5H_4Br_2O_3 + 2\,Br_2 + H_2O = C_4HBr_3O_2 + CO_2 + 3\,HBr.$$
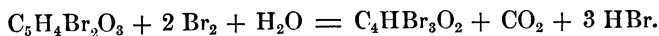
Mucobromylbromide is so slowly attacked by water that little muco-bromic acid could have been formed under the conditions chosen; but it is found in abundance when the product of the reaction stands for a long time in dilute solution. The alcoholic mother liquors obtained from the recrystallization of the mucobromylbromide were evaporated, and the residue boiled with water under a reverse cooler until the bromanhydride had been converted into mucobromic acid. A small amount of insoluble material was then left, which had the odor of tetrabromfurfuran, but we were unable to identify it with precision. A preliminary experiment under essentially the same conditions had already yielded us a crystalline body, which was proved by its melting

point (64°), and other characters, to be tetrabromfurfuran. Hill and Sanger * had previously found that this substance was formed in considerable quantities when bromine was gradually added to the dibrompyromucic acid suspended in water.

Action of Oxidizing Agents.

As we already have said, dibromcrotonolactone may be crystallized without alteration from concentrated nitric acid, but on long boiling it is slowly oxidized, and mucobromic acid or dibrommaleic acid formed. Even fuming nitric acid attacks it with difficulty, and after boiling for half an hour the greater part of the lactone taken may be recovered unchanged. We dissolved the lactone in 8 times its weight of concentrated nitric acid (sp. gr. 1.42), and boiled the solution for three hours under a reverse condenser. The unaltered lactone was then driven off with steam, and the acid solution evaporated to small volume. On cooling, mucobromic acid separated in abundance, which melted at 119–120°, after recrystallization from hot water. Even after boiling for six hours with concentrated nitric acid the oxidation was far from complete, but it was then easy to establish the formation of dibrommaleic acid through the melting point (114–115°) of its anhydride. On boiling the lactone with bromine water, it is slowly converted into mucobromic acid. The reaction may be hastened greatly by using concentrated hydrobromic acid as a solvent, and the oxidation is then completed in a comparatively short time. The mucobromic acid which we obtained, when recrystallized from water, melted at 120–121°. With chromic acid the action is also very slow, and we have been unable to identify any products of the oxidation except carbonic dioxide. If an amount of chromic acid was used which corresponded to one atom of oxygen for each molecule of the lactone, several hours at 100° were needed for the complete reduction of the chromic acid. On distillation large quantities of the unaltered lactone were obtained (melting point 90–91°), and the retort residue, when evaporated to small volume, deposited nothing on cooling. This residue was therefore extracted with ether, the ethereal extract shaken with a dilute solution of sodic carbonate, and this alkaline solution immediately acidified with hydrochloric acid, and again extracted with ether. The ether then left upon evaporation a small syrupy residue, which was strongly acid to test paper. After standing for several days, several minute clusters of rhombic plates could be seen under

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* These Proceedings, XXI. 172.

the microscope. In appearance they closely resembled mucobromic acid, but they were insufficient in quantity even for a melting point determination. Since the dibromcrotonolactone reduced an ammoniacal solution of argentic nitrate on heating, we made one attempt to effect its oxidation with argentic oxide. On boiling an aqueous solution of the lactone with a large excess of well washed argentic oxide, metallic silver was formed, but at the same time argentic bromide in large quantity. An approximate quantitative determination showed that 87.5 per cent of the total bromine contained in the lactone had been converted into argentic bromide. After a careful search we failed to find any products of the oxidation except an. amount of dibrommaleic acid, which was just sufficient for its complete identification through the microscopic appearance of its barium salt and the melting point of its anhydride, 114–115°.

Action of Bromine.

Dibromcrotonolactone is not attacked by bromine at ordinary temperatures, but at 100° substitution is quite rapidly effected. If equal molecules of bromine and the lactone are taken, a colorless oil is obtained after several hours' heating, which on standing gradually solidifies, and the crystalline solid may be purified by recrystallization from small quantities of alcohol. The substance which was thus obtained melted at 56–57°, and gave with alkalies in alcoholic solution the characteristic blue color described by Hill and O. R. Jackson.* Mucobromylbromide had therefore been formed from the dibromcrotonolactone according to the equation

$$C_4H_2Br_2O_2 + Br_2 = C_4HBr_3O_2 + HBr.$$
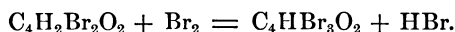
When heated with an excess of bromine further substitution is effected and a product is obtained in which both the hydrogen atoms of the dibromcrotonolactone are replaced. For the preparation of this body we heated equal molecules of mucobromylbromide and bromine in sealed tube at 125–130°. At this temperature the reaction proceeds rapidly, but it is also completed at 100° on longer heating. The colorless oil which we obtained gave no blue color in alcoholic solution with sodic carbonate, and on standing gradually solidified. The carefully pressed solid proved to be extremely soluble in alcohol, ether, chloroform, benzol, or carbonic disulphide, but it was somewhat more sparingly soluble in ligroin and could be purified by recrystalli-

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* These Proceedings, XVI. 175.

zation from this solvent. The percentage of bromine which the substance contained corresponded to the formula $C_4Br_4O_2$.

   I. 0.1685 grm. substance gave 0.3177 grm. AgBr.
   II. 0.1884 grm. substance gave 0.3552 grm. AgBr.

	Calculated for $C_4Br_4O_2$.	Found. I.	II.
Br	80.00	80.23	80.20

This substance crystallizes from ligroin in clustered leaflets which melt at 58–59°. It has a strong suffocating odor like that of the acid bromanhydrides. When heated with water it is slowly dissolved and the solution then contains dibrommaleic acid. The acid was as usual identified by the crystalline form of the barium salt, and by the melting point (114–115°) of its anhydride. On treating the body with stannous chloride and hydrochloric acid the dibromcrotonolactone is again formed by reduction. The mode of formation, the composition, and the behavior of this body justify the conclusion that it is the unsymmetrical form of dibrommaleylbromide. Its behavior will be further studied in this Laboratory. We have made many unsuccessful attempts to prepare an identical or an isomeric body directly from dibrommaleic acid. We have tried the action of phosphoric pentabromide upon dibrommaleic anhydride at temperatures which varied from 100° to 225°, and either obtained the unaltered anhydride, or else carbonization ensued. We were equally unsuccessful in our attempts to prepare such a product through the salts of the acid.

Action of Aniline.

Aniline reacts upon the $\alpha\beta$-dibromcrotonolactone at ordinary temperatures and forms α-phenylamido-β-bromcrotonolactone. This substance is most readily prepared by dissolving the lactone in twenty parts of alcohol, diluting this solution with an equal weight of water, and then adding somewhat more than two molecules of aniline. On standing long needles of the aniline derivative separate in abundance, which may be purified by recrystallization from sixty per cent acetic acid, and afterward from alcohol.

   I. 0.2570 grm. substance gave 0.4426 grm. CO_2 and 0.0763 grm. H_2O.
   II. 0.2393 grm. substance gave 0.1775 grm. AgBr.
  III. 0.2727 grm. substance gave 13.4 c.c. of moist nitrogen at 21° and under a pressure of 763 mm.

	Calculated for $C_{10}H_8BrNO_2$	I.	Found. II.	III.
C	47.24	46.97		
H	3.15	3.30		
Br	31.50		31.56	
N	5.51			5.63

a-Phenylamido-β-bromcrotonolactone is almost insoluble in ether, carbonic disulphide, or ligroin, but dissolves somewhat more readily in boiling benzol or chloroform. It is somewhat sparingly soluble even in boiling alcohol, still less freely in boiling water, and as the solutions cool is deposited in each case in long brilliant needles. In hot glacial acetic acid the substance dissolves readily; from chloroform it crystallizes in thin transparent plates. When slowly heated it melts with decomposition at about 165°, but if the capillary tube containing the substance is plunged into the heated bath it melts promptly at 186–187° and immediately decomposes. In alkaline solutions it dissolves readily on warming, and if the solution be quickly cooled it crystallizes out apparently unchanged, but on heating for a longer time decomposition ensues, as the strong odor of phenylisocyanide shows. By the action of sodium amalgam bromine is removed and a-phenylamidocrotonolactone, which we shall describe later, is formed. We have been unable to replace the second atom of bromine by heating with an excess of aniline.

Action of Hydriodic Acid.

When $a\beta$-dibromcrotonolactone is dissolved in ordinary distillable hydriodic acid and the solution is boiled for a short time, or heated for a longer time at 100°, one atom of bromine is replaced by iodine, and as the solution cools the a-iod-β-bromcrotonolactone separates in long prisms. This same body is also formed by the action of phosphorous iodide upon mucobromic acid or when hydriodic acid acts upon mucobromylbromide, and it may easily be made the chief product of the latter reaction. For analysis it was recrystallized from alcohol.

I. 0.2393 grm. substance gave 0.1453 grm. CO_2 and 0.0229 grm. H_2O.

II. 0.1874 grm. substance gave 0.2747 grm. $AgBr + AgI$.

III. 0.2031 grm. substance gave 0.2978 grm. $AgBr + AgI$.

	Calculated for $C_4H_2BrIO_2$.	I.	Found. II.	III.
C	16.61	16.56		
H	0.69	1.05		
Br + I	71.63		71.76	71.78

The a-iod-β-bromcrotonolactone is quite readily soluble in benzol or chloroform, more sparingly soluble in ether, carbonic disulphide, or ligroin. It dissolves freely in boiling alcohol, and as the solution cools it is deposited in quite large, oblique, colorless prisms, which gradually change color on exposure. With steam it distils with difficulty. The melting point of most preparations of this substance we have found to be constant at 118–119°. Still we were frequently unable to raise by recrystallization alone the melting point of material which melted at too low a temperature, and on one occasion a preparation made in the usual way melted one degree higher at 119–120°. Toward aqueous alkalies this substance behaves like the corresponding bromine derivative, an alkaline iodide being formed in the decomposition. Concentrated nitric acid or bromine water on boiling liberates iodine. When heated with one molecule of dry bromine in sealed tube at 100°, iodine is also liberated, and but a small quantity of hydrobromic acid is formed. With aniline in dilute alcoholic solution it yields the a-phenylamido-β-bromcrotonolactone, which has already been described, although not quite as smoothly as the dibromlactone, since dark-colored viscous products, which we have not further examined, are formed at the same time. On reduction with zinc dust and glacial acetic acid, the β-bromcrotonolactone melting at 58°, which we shall presently describe, was formed. After dilution with water the acid solution was extracted with ether, the ethereal extract washed with a dilute solution of sodic carbonate, and the crystalline residue obtained by the evaporation of the ether recrystallized several times from small quantities of alcohol. The body thus obtained had the properties of the β-bromcrotonolactone, melted at 57–58°, contained but an unweighable trace of iodine, and gave on analysis the required percentage of bromine.

0.2078 grm. substance gave 0.2407 grm. AgBr.

	Calculated for $C_4H_3BrO_2$.	Found.
Br	49.08	49.27

When the iodbromcrotonolactone was boiled with hydriodic acid the separation of iodine soon ensued. After long boiling with the addition of red phosphorus, although traces of volatile products, which had the odor of fat acids, had been formed, the main product of the reduction was a viscous oily body, which could be extracted by ether from the diluted solution, but from which we were unable to prepare any material suitable for analysis. With distillable hydriodic acid and red phosphorus in sealed tubes at temperatures below 180° we

obtained substantially the same result, while prolonged heating at 200°
brought about decomposition. We had no better success when we
employed hydriodic acid saturated at 0°, although in this case decom-
position set in at a lower temperature.

β-BROMCROTONOLACTONE.

When $\beta\delta$-dibrompyromucic acid is boiled with concentrated hydro-
bromic acid, it is slowly decomposed, carbonic dioxide is evolved, and
β-bromcrotonolactone is formed. The reaction does not run as
smoothly as it does with tribrompyromucic acid, and more or less car-
bonization ensues. When the reaction appears to be completed, the
dilution of the dark brown solution usually precipitates a small amount
of dark-colored unaltered acid, but no lactone is thus thrown down.
The filtered solution is then extracted with ether, the ethereal extract
washed with a dilute solution of sodic carbonate, and dried with calcic
chloride. The residue left after distilling off the ether gradually
solidifies on standing, and the crude product, which amounts to about
one quarter of the dibrompyromucic acid taken, may be recrystallized
from small quantities of alcohol or from ether. The same body may
be prepared much more conveniently by the reduction of the $a\beta$-di-
bromcrotonolactone with zinc dust and acetic acid. The dibromcro-
tonolactone is suspended in its own weight of 80 per cent acetic
acid, and somewhat more than the calculated weight of zinc dust is
then added with careful cooling. At first the reduction proceeds rap-
idly with the evolution of heat, but several hours at ordinary tempera-
tures are necessary for its completion. When the zinc has nearly
disappeared the viscous solution is warmed, filtered, and the clear fil-
trate cautiously diluted with water. The bromlactone is thus precipi-
tated as an oil, which after cooling and shaking soon solidifies in the
form of colorless feathery crystals. The precipitated lactone amounts
to 45 per cent of the weight of the dibromcrotonolactone taken, and
somewhat more may be obtained by extracting the mother liquor
with ether.

I.   0.2417 grm. substance gave 0.2609 grm. CO_2 and 0.0440 grm. H_2O.
II. 0.1913 grm. substance gave 0.2214 grm. AgBr.

	Calculated for $C_4H_3BrO_2$.	I.	II.
		Found.	
C	29.45	29.44	
H	1.86	2.02	
Br	49.08		49.24

The β-bromcrotonolactone is readily soluble in alcohol, chloroform, benzol or carbonic disulphide. It is decidedly less soluble in ether, and very sparingly soluble in ligroin. From small quantities of alcohol it crystallizes in colorless clustered prisms, from ether by slow evaporation in large transparent six-sided plates. It is quite readily soluble in hot water, and as the hot aqueous solution cools it separates in clear obliquely truncated prisms. It melts at 58°, and boils under a pressure of 18 mm. at 140°. It distils with steam, although with some difficulty. Aqueous alkalies dissolve it with the formation of a deep yellow color, and the solution then contains an alkaline bromide. In dilute alcoholic solution aniline also removes bromine, but forms at the same time a dark-colored viscous oil, from which we have been able to isolate no crystalline product.

Action of Bromine.

β-Bromcrotonolactone is but slowly attacked by bromine in the cold. If one molecule of bromine is added to the powdered lactone, a clear deep red solution is soon obtained, but the color fades so slowly that several days are required to complete the reaction at ordinary temperatures. On opening the tube a small quantity of hydrobromic acid escaped, but the weight of the crystalline product was substantially the same as that of the materials employed. After several recrystallizations from alcohol an analysis also showed that the substance had been formed by the addition of bromine.

0.2965 grm. substance gave 0.5175 grm. AgBr.

	Calculated for $C_4H_3Br_3O_2$.	Found.
Br	74.30	74.27

This body, which from the mode of its formation must be the $a\beta_2$-tribrombutyrolactone, is readily soluble in alcohol, ether, benzol, carbonic disulphide, or chloroform, but is more sparingly soluble in ligroin. From alcohol it is deposited in large, well formed, brilliant prisms, which melt at 63–64°. On boiling with water a part distils unchanged, but decomposition soon sets in, carbonic dioxide is evolved, and hydrobromic acid is formed. If the β-bromcrotonolactone is heated to 100° with one molecule of bromine, the color of the bromine soon disappears, but at the same time hydrobromic acid is formed in considerable quantities. With an excess of bromine at 100° mucobromylbromide is formed in abundance. The product which we obtained melted at 56–57°, gave in alcoholic solution a deep blue color with sodic carbonate, and when heated with water yielded mucobromic acid.

Action of Oxidizing Agents.

We have been unable to obtain any characteristic products by the oxidation of the β-bromcrotonolactone. On boiling with concentrated nitric acid oxidation takes place, but carbonic dioxide is evolved in abundance, and no other definite products were isolated. When heated with bromine in aqueous solution the addition product is apparently formed at first, but on boiling this is soon broken up with the evolution of carbonic dioxide. We also noticed in this case the formation of a small amount of a highly crystalline body which on recrystallization from alcohol formed long lustrous prisms. The melting point (54°), the camphor-like odor, and other physical properties, render it extremely probable that this substance was pentabromethan, but it was insufficient in quantity for analysis. The aqueous solution upon evaporation gave a small viscous residue, from which on long standing a few microscopic rhombic plates separated which appeared to be mucobromic acid.

a-Bromcrotonolactone.

Since the $\gamma\delta$ dibrompyromucic acid is as yet unknown, and the a bromine atom of the $a\beta$-dibromcrotonolactone seems always to be first attacked by reagents, it was necessary to try some new method for the preparation of the a-bromcrotonolactone. It occurred to us that it was by no means impossible that it might be made from brommaleylbromide, since the chloranhydrides of similar dibasic acids were known in several instances to yield lactones on reduction. We soon found on trial that our conjecture was correct. Hill and Sanger [*] had already shown that a crystalline body having the formula $C_4HBr_3O_2$, and yielding monobrommaleic acid when decomposed by water, could be made from $\beta\delta$-dibrompyromucic acid by the action of bromine in aqueous solution. This brommaleylbromide we therefore prepared, although we modified slightly the method of preparation in that we dissolved the $\beta\delta$-dibrompyromucic acid in the requisite amount of a dilute solution of sodic carbonate, and added to this feebly alkaline solution slightly more than two molecules of bromine. We attempted to purify the product by distillation *in vacuo*, and found that it boiled without noticeable decomposition at 124–125° under a pressure of 17 mm. The distillate remained liquid for a long time, and then but

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[*] These Proceedings, XXI. 166.

partially solidified with the separation of the original substance. The solid portion melted at 54–55°, while the brommaleylbromide, according to Hill and Sanger, melts at 55–56°. The liquid portion was much more readily attacked by cold water than the original substance, and gradually dissolved, leaving about one third its weight of the crystalline solid, which had been held in solution. In the aqueous solution was found monobrommaleic acid melting at 130°, and by evaporation monobromfumaric acid melting at 178° was obtained. These facts seem to us sufficient to show that we had in our hands two different bodies, each of which showed the properties of a brommaleylbromide. The relation between these bodies will be more fully investigated. For the preparation of the *a*-bromcrotonolactone we found that no purification of the crude product was necessary.

The brommaleylbromide is readily reduced by a solution of stannous chloride in strong hydrochloric acid, but the isolation of the lactone which is formed is difficult. Although it is volatile with steam, it distils slowly, remains dissolved in the distillate, and must be extracted from the dilute solution by ether. We have found it more convenient to use zinc and acetic acid for the reduction. The brommaleylbromide is suspended in one and a half times its weight of 80 per cent acetic acid, and somewhat more than the calculated amount of zinc dust added with careful cooling. The reaction is at first attended with great evolution of heat, and the zinc dust must be slowly added. After the completion of the reaction the addition of water to the filtered solution precipitates but a small part of the lactone, and the solution must be thoroughly extracted with ether. The ethereal solution, when washed with a dilute solution of sodic carbonate and dried with calcic chloride, leaves upon distillation the beautifully crystalline *a*-bromcrotonolactone contaminated with but small amounts of oily impurities. The thoroughly pressed substance may most readily be purified by recrystallization from ether. This same *a*-bromcrotono-lactone is also formed by the action of bromine in aqueous solution upon *β*-brompyromucic acid. As is the case with the analogous reaction by which *aβ*-dibromcrotonolactone is formed from *βγ*-dibrompyromucic acid, the yield is small, and we have as yet merely satisfied ourselves of the identity of the product through its physical properties.

0.2000 grm. substance gave 0.2304 grm. AgBr.

	Calculated for $C_4H_3Br O_2$.	Found.
Br	49.08	49.01

The a-bromcrotonolactone is readily soluble in alcohol or chloroform, somewhat more sparingly soluble in ether or benzol, sparingly soluble in cold carbonic disulphide, more readily in hot, and sparingly soluble in ligroin. It dissolves quite freely in boiling water and distils slowly with steam. It crystallizes in long transparent prisms of adamantine lustre, which melt at 77°. It dissolves in alkalies with a deep yellow color and the formation of an alkaline bromide. It also reduces argentic nitrate in ammoniacal solution on boiling. With aniline, when dissolved in dilute alcohol, it gives the well crystallized a-phenylamidocrotonolactone. The a-bromcrotonolactone appeared to be identical with the body of like formula and the same melting point which Hill and Sanger * obtained in small quantity as a by-product in the preparation of the dibrompyromucic acids by the action of alcoholic sodic hydrate upon pyromucic tetrabromide. Still their statements concerning the behavior of their substance toward bromine were at variance with our own observation, and a more vigorous proof of the identity of the two bodies was necessary. Fortunately a small amount (0.125 grm.) of their old preparation still remained, and we were able to establish its identity with our own product, since it gave with aniline the same a-phenylamidocrotonolactone melting at 217–218°,† and was attacked by bromine and water in the same way.

Action of Bromine.

a-Bromcrotonolactone is very slowly attacked by dry bromine at ordinary temperatures. If one molecule is added, the lactone does not dissolve at first, and the color of the bromine remains apparently unchanged for several days. The reaction then seems to proceed more rapidly, and at the end of the sixth day we found that the color had faded completely. The tube then opened with pressure, and a large amount of hydrobromic acid escaped. Substitution had evidently taken place, and the weight of the liquid product corresponded precisely with that which would theoretically be required by the replacement of one hydrogen atom by bromine. The product of the reaction remained for a long time liquid, and its alcoholic solution gave but a greenish color on the addition of sodic carbonate. After long standing in desiccator a few large clear crystals appeared, which from their melting point (90–91°) and other characters were shown to be the aβ-dibromcrotonolactone. After distilling with steam, in order to remove the dibromcrotonolactone, the aqueous solution left on

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* These Proceedings, XXI. 158.   † See page 31.

evaporation a viscous residue. After long standing in desiccator a few microscopic rhombic plates appeared, which were doubtless muco-bromic acid. On repeating this experiment later, when the mean temperature of the room was much higher, the reaction was com-pleted in about half the time, the product gave a decided blue color in alcoholic solution with sodic carbonate, showing the formation of mucobromylbromide, but on long standing crystals of dibromcrotono-lactone were also formed. On heating with two molecules of bromine for several hours at 100°, mucobromylbromide is formed in quantity. The product gradually solidified on standing, gave an intense blue color with sodic carbonate, and after recrystallization from alcohol melted at 56–57°.

Action of Oxidizing Agents.

Concentrated nitric acid oxidizes the α-bromcrotonolactone without much difficulty at 100°. Carbonic dioxide is freely evolved, and a small quantity of a volatile oil is formed, which has a suffocating, sharp odor, and contains both nitrogen and bromine. We were un-able to isolate other characteristic products of the reaction. With bromine in aqueous solution we had somewhat better success. The reaction progressed slowly, but after boiling for several hours with an excess of bromine a small amount of an oily product had been formed which was not further examined. The aqueous solution upon evapo-ration gave characteristic crystals of mucobromic acid, which, after re-recrystallization from water, melted at 120–121°. The weight of mucobromic acid thus obtained was, however, barely 20 per cent of the theoretical amount, and carbonic dioxide was also formed in the reaction. Hill and Sanger had found that the body which they de-scribed as having the composition of a bromcrotonolactone and melt-ing at 77° was converted by bromine and water into an amorphous substance insoluble or sparingly soluble in all common solvents. Two experiments which we tried with small quantities of their old prepa-ration failed to confirm their statements. It gave precisely the same results which we had already obtained with the α-bromcrotonolactone. The yield of mucobromic acid given by the reaction is so small, and the quantity of the old material at our disposal was so limited, that we were unable to purify our product sufficiently for a sharp deter-mination of the melting point. Its appearance and behavior left no doubt as to its identity.

Action of Aniline.

If aniline is added to a solution of the a-bromcrotonolactone in dilute alcohol, the bromine is gradually displaced at ordinary temperatures, and the corresponding phenylamidocrotonolactone is formed. The somewhat dark-colored crystalline mass, which separates after the lapse of twenty-four hours, may be purified by recrystallization from glacial acetic acid, and afterward from alcohol. The a-chlorlactone which was described by Hill and L. L. Jackson,[*] and of which we shall speak later, also reacts as readily ,with aniline, and naturally gives the same product. The same body may furthermore be made, although with more difficulty, by the reduction of the a-phenylamido-β-bromcrotonolactone. The elimination of the bromine takes place so slowly in acid solution that we have found it more advantageous to employ sodium amalgam with dilute alcohol, and to allow the reduction to proceed in alkaline solution at ordinary temperatures. Although more or less decomposition of the phenylamidobromcrotonolactone takes place, as the strong odor of phenylisocyanide which is developed shows, a satisfactory product is obtained in this way. The finely powdered a-phenylamido-β-bromcrotonolactone is suspended in 50 times its weight of about 60 per cent alcohol, and an excess of sodium amalgam containing 2 per cent of metallic sodium is added. The substituted lactone gradually goes into solution, and we usually have found the reduction complete at the end of four or five hours. The clear solution is then acidified with acetic acid, the alcohol driven off upon the water bath, and the crystalline product which separates recrystallized from glacial acetic acid. Occasionally we have found it necessary to treat the product a second time with sodium amalgam in order to remove the last traces of bromine.

I. 0.1991 grm. substance gave 0.4996 grm. CO_2 and 0.0962 grm. H_2O.

II. 0.2114 grm. substance gave 14.9 c.c. of moist nitrogen at $21°.3$ and under a pressure of 754 mm.

	Calculated for $C_{10}H_9NO_2$.	Found. I.	II.
C	68.57	68.42	
H	5.14	5.36	
N	8.00		7.94

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[*] These Proceedings, XXIV. 353.

α-phenylamidocrotonolactone is very sparingly soluble even in boiling water. It dissolves quite readily in boiling alcohol, more sparingly in cold, and very sparingly in hot benzol or chloroform; in ether, ligroin, or carbonic disulphide, it is nearly insoluble. It is readily soluble in hot glacial acetic acid, and crystallizes on cooling in feather-formed aggregations of branching needles. The melting point of the substance varies somewhat according to the rapidity with which it is heated; but with proper care to avoid long heating it was found to melt quite sharply at 217–218°, although decomposition ensued on further heating. Material made from the α-chlor- and α-bromlactones, as well as by the reduction of the phenylamidobromlactone, showed identically the same behavior on heating, and when tested side by side in the same bath melted at the same temperature. The body dissolves readily in hot concentrated hydrochloric acid, but aniline seems to be formed at once. In hot alkaline solutions it dissolves somewhat more readily than in water, and if such a hot solution is quickly cooled it separates apparently unchanged. On longer heating decomposition sets in. A solution of the body in hot dilute baric hydrate was boiled for a short time and distilled. The distillate contained aniline in abundance, as was shown by the formation of tribromaniline melting at 118–119°. At the same time baric carbonate had been precipitated, and in solution was found a barium salt which was extremely soluble in water, was precipitated by alcohol from the concentrated aqueous solution in an amorphous form, and was left as a brownish varnish upon evaporation.

REDUCTION OF THE αβ-DIBROMCROTONOLACTONE TO CROTONOLACTONE.

When dibromcrotonolactone is heated to 100° with dilute sulphuric acid and granulated zinc, it is rapidly reduced, and at the end of several hours the reduction is complete. It was easy to prove by quantitative determinations that all the bromine of the original substance had been converted into hydrobromic acid, and the behavior of the solution toward decinormal potassic hydrate also showed that it contained a lactone in nearly theoretical quantity. We found it practically impossible to extract the lactone from aqueous solution, and we therefore distilled this solution in a current of steam. The distillate which we obtained was feebly acid, but it also contained a small quantity of a lactone, which, however, we found by titration to be relatively large in proportion to the free acid. The amount of free acid varied

very much in our preparations, and apparently disappeared entirely, if during the reduction too large an excess of sulphuric acid was not used. With ordinary care the free acid did not correspond to as much as one tenth of the total alkali which was neutralized on boiling, and we were unable to increase that amount beyond one fifth by any modification of the mode of reduction. Our determinations furthermore showed that each litre of distillate could contain but 1.25 grm. of crotonolactone if this body had really been formed by reduction. We made many fruitless attempts to isolate the crotonolactone from this dilute aqueous solution, and since our main object was to establish beyond question the lactone nature of the dibromcrotonolactone from which it had been formed, we proceeded at last to prepare from the solution a salt of the corresponding oxycrotonic acid. To the dilute lactone solution we added slightly more than the required amount of baric hydrate, heated the alkaline solution to boiling, precipitated after the lapse of some time the slight excess of baric hydrate by carbonic dioxide, and evaporated to small volume the filtered solution. We obtained in this way a somewhat brown syrupy residue, which on drying yielded a hard varnish. For its purification it was dissolved in a small amount of water, and alcohol added until a portion of the salt had been precipitated. The filtered solution was then concentrated by evaporation, a trace of a haloid barium salt removed by the cautious addition of argentic carbonate, and the clear solution evaporated upon the water bath. After drying for some time at 100°, the gummy salt became sufficiently friable to enable us to powder it, and it was then thoroughly dried at 100°. A complete analysis showed that this salt had the composition of a baric oxycrotonate. The second determination of carbonate was made in the wet way by the method of Messinger,[*] the first by the more usual method with potassic dichromate in open tube.

I.   0.1961 grm. salt gave 0.2044 grm. CO_2 and 0.0694 grm. H_2O.
II.   0.1432 grm. salt gave 0.1503 grm. CO_2.
III.   0.2414 grm. salt gave 0.1655 grm. $BaSO_4$.

	Calculated for $Ba(C_4H_5O_3)_2$.	I.	Found. II.	III.
C	28.30	28.42	28.63	
H	2.95	3.93		
Ba	40.44			40.33

* Berichte d. deutsch. chem. Gesellsch., XXI. 2910.

The formation of the crotonolactone through the reduction of the dibromcrotonolactone was thus established. Since the salts of the oxycrotonic acid all seemed to possess the same uninviting properties, and our main end was already reached, we made no further study of them.

$a\beta$-DICHLORCROTONOLACTONE.

The $a\beta$-dichlorcrotonolactone may be prepared most easily by the reduction of mucochlorylbromide. This body, which has not yet been described, was readily made by the action of phosphorous tribromide upon mucochloric acid. The reaction ran perfectly smoothly, and but little more than one molecule of phosphorous tribromide was needed for complete reaction with three molecules of mucochloric acid. After heating at 100° until the liquefied product grew turbid with the separation of phosphorous acid, the flask was well cooled, and cold water added with constant shaking. The oil which separated gradually solidified, and the granular product which was obtained could readily be collected by filtration. As in the preparation of mucobromylbromide we have found it easy to obtain 88–90 per cent of the theoretical yield, and the crude product was sufficiently pure for further use. An analysis of a sample recrystallized from ligroin gave the required percentage of halogen.

0.2721 grm. substance gave 0.5556 grm. AgCl + AgBr.

	Calculated for $C_4HCl_2O_2Br$.	Found.
Cl + Br	65.09	64.91

Mucochlorylbromide is very readily soluble in alcohol, ether, chloroform, carbonic disulphide, or benzol ; in ligroin it is somewhat more sparingly soluble. From a solution in dilute alcohol it may be obtained by spontaneous evaporation in large transparent plates which melt at 36°. In alcoholic solution it gives with dilute alkalies a deep purple color, which rapidly passes into a wine-red and finally to yellow. With sodic carbonate we have also frequently noticed the formation of a deep green color after the wine-red.

The reduction of the mucochlorylbromide is easily effected by means of stannous chloride and hydrochloric acid. The reaction proceeds slowly in the cold, but may be carried to the end at ordinary temperatures. On warming gently it runs rapidly with the evolution of heat, and in a short time, if the reaction is promoted by vigorous shaking, the mucochlorylbromide completely disappears. On cooling and adding water the dichlorlactone separates in long slender needles, while

the mother liquor yields on distillation with steam a small quantity of the same body.   The yield amounts to 78 per cent of the weight which could theoretically be obtained from the mucochlorylbromide, or, taking both reactions into account, 70 per cent of the amount which the mucochloric acid employed should give.   The substance recrystallized from ligroin gave on analysis the following results : —

I.   0.4362 grm. substance gave 0.4955 grm. CO_2 and 0.0574 grm. H_2O.
II.   0.3097 grm. substance gave 0.5789 grm. AgCl.

	Calculated for $C_4H_2Cl_2O_2$.	Found. I.	II.
C	31.37	30.97	
H	1.31	1.46	
Cl	46.40		46.21

This dichlorcrotonolactone we have also made by the decomposition of trichlorpyromucic acid, and by the action of bromine water upon $\beta\gamma$-dichlorpyromucic acid.   Trichlorpyromucic acid appears to be more stable than tribrompyromucic acid.   Still it is slowly decomposed with the evolution of carbonic dioxide, when heated to boiling with 50 per cent sulphuric acid, and the dichlorlactone is formed.   We have made by this method only a sufficient quantity of material to enable us to identify it with precision.   In studying the action of bromine upon $\beta\gamma$-dichlorpyromucic acid we followed the same method that we had employed with the $\beta\gamma$-dibrompyromucic acid, and found that the reaction followed precisely the same course.   In this case, however, we proved the presence of mucochlorylbromide among the insoluble products of the reaction only through the characteristic color which was developed upon the addition of sodic carbonate to the alcoholic solution. The dichlorlactone was isolated from the aqueous solution by distillation with steam, as well as by extraction with ether.   Its identity was proved by its melting point, and by its conversion into a-phenylamido-β-chlorcrotonolactone melting at 183°.*

$a\beta$-Dichlorcrotonolactone is very readily soluble in benzol or chloroform, readily in alcohol or ether, somewhat more sparingly soluble in carbonic disulphide, and sparingly soluble in cold ligroin, although more freely soluble in hot.   It dissolves quite readily in boiling water, and volatilizes freely with steam.   The substance crystallizes ordinarily in long silky needles, but on slow evaporation of the ethereal solution it is deposited in clear six-sided plates.   It melts at 50–51°, and boils

* See page 36.

under a pressure of 18 mm. at 114–115° without noticeable decomposition. With aqueous alkalies it behaves like the corresponding bromine compound, and gives a bright yellow solution. Hydroxylamine has no action upon it, and phenylhydrazine removes chlorine without forming any crystalline product. Aniline when added to its solution in dilute alcohol gives the highly crystalline a-phenylamido-β-chlorcrotonolactone. Hydriodic acid gives at 100° the a-iod-β-chlorcrotonolactone.

Action of Oxidizing Agents.

a-β-Dichlorcrotonolactone is oxidized with even more difficulty than the corresponding dibromlactone. After boiling for several hours with eight times its weight of concentrated nitric acid (sp. gr. 1.42), a large part of the lactone remained unaltered, and could be recovered by distillation with steam. The aqueous solution was then evaporated to dryness on the water bath, and the crystalline residue treated with small quantities of cold water. Mucochloric acid was then left behind, which after recrystallization from hot water melted at 124–125°. The cold water had taken up a small quantity of a readily soluble acid, which undoubtedly was dichlormaleic acid. Since mucochloric acid yields dichlormaleic acid on oxidation with nitric acid, although it is attacked with more difficulty than mucobromic acid, it did not seem to us worth while to take further steps for its preparation in larger quantity and identification. Bromine dissolved in concentrated hydrochloric acid oxidizes the dichlorlactone, although in this case also long continued boiling is required to complete the reaction.

Action of Aniline.

Aniline readily reacts upon the aβ-dichlorcrotonolactone at ordinary temperatures, and forms the a-phenylamido-β-chlorcrotonolactone. The reaction runs best with a dilute solution in 50 per cent alcohol, and on standing the product separates in broad glistening leaflets, which are more or less highly colored. This color may be removed by recrystallization from glacial acetic acid or from alcohol.

0.1491 grm. substance gave 0.1011 grm. AgCl.

	Calculated for $C_{10}H_8ClNO_2$.	Found.
Cl	16.91	16.76

a-Phenylamido-β-chlorcrotonolactone is quite readily soluble in boiling alcohol, and but sparingly soluble in cold. It also dissolves quite freely in boiling chloroform or benzol, more sparingly in ether or

carbonic disulphide, and is almost insoluble in ligroin. It is very sparingly soluble in boiling water, and is deposited in the form of fine needles as the solution cools. From chloroform it crystallizes in clear flat prisms, which melt quite sharply at 183°, although decomposition sets in at a somewhat higher temperature. Toward alkalies it behaves like the corresponding bromine derivative. It dissolves more freely in dilute sodic hydrate on heating than in water, and, if this solution is quickly cooled, it crystallizes out apparently unchanged. On longer heating decomposition ensues with the formation of phenylisocyanide.

Action of Hydriodic Acid.

The action of hydriodic acid upon the $\alpha\beta$-dichlorcrotonolactone we have studied only so far as to prove that α-iod-β-chlorcrotonolactone is formed. This body we have also made directly from mucochloryl-bromide by the action of hydriodic acid at 100°. In order to keep up the strength of the hydriodic acid we found it advantageous to add at the same time potassic iodide and red phosphorus. The product was precipitated by the addition of water decolorized with sulphurous acid and recrystallized from alcohol.

0.2015 grm. substance gave 0.3116 grm. $AgCl + AgI$.

	Calculated for $C_4H_2ClIO_2$.	Found.
$Cl + I$	66.45	66.36

α-Iod-β-chlorcrotonolactone dissolves very readily in benzol, is freely soluble in ether, but is more sparingly soluble in chloroform or carbonic disulphide. It dissolves easily in hot alcohol, but as this solution cools the greater part separates in long flattened needles which melt at 108–109°. In its behavior toward reagents it closely resembles the bodies of similar constitution already described.

β-CHLORCROTONOLACTONE.

By the action of zinc dust and glacial acetic acid the $\alpha\beta$-dichlor-crotonolactone may be reduced without difficulty to the β-chlorcro-tonolactone, but the physical properties of the latter body make its isolation a little more troublesome than that of the corresponding body containing bromine. We dissolved the dichlorcrotonolactone in nearly twice its weight of 80 per cent acetic acid, and slowly added with cooling somewhat more than the theoretical quantity of zinc dust. The reduction was at first attended with the evolution of heat, but afterward became sluggish. After standing over night, the

viscous solution, in which some metallic zinc was still suspended, was warmed, filtered, and the clear filtrate diluted with water. As the oil which was then precipitated showed no tendency to crystallize when cooled and scratched, the whole was extracted with ether, the ethereal solution washed with a dilute solution of sodic carbonate, dried with calcic chloride, and the ether removed by distillation. The liquid residue left by the ether was then distilled under diminished pressure. After two distillations the greater part of the product was collected between 128° and 130°, under a pressure of 22 mm., and on cooling this fraction to 10° the larger portion of it solidified. The solid was drained on the pump in a Gooch crucible, and carefully pressed with filter paper. This perfectly dry material was then melted, cooled, and the crystalline solid again pressed, and these operations repeated for a second time without raising perceptibly the melting point. An analysis showed that the body was a chlorcrotonolactone.

<center>0.3071 grm. substance gave 0.3720 grm. AgCl.</center>

	Calculated for $C_4H_3ClO_2$.	Found.
Cl	29.95	29.95

The β-chlorcrotonolactone is very readily soluble in alcohol, ether, chloroform, or benzol; less soluble in carbonic disulphide, and sparingly soluble in ligroin. It may be crystallized most conveniently by strongly cooling the ethereal solution after the addition of ligroin. It crystallizes in well-formed flat prisms, which melt at 25–26°. The boiling point of the pure substance was found to be 124–125° under a pressure of 18 mm. It is quite freely soluble in hot water, and distils slowly with steam. Toward the alkaline hydrates and aniline it behaves like the β-bromcrotonolactone. We have not yet studied its behavior toward bromine or oxidizing agents. Although the $\beta\delta$-dichlorpyromucic acid is an extremely expensive substance on account of the difficulties which lie in the way of its preparation, and the small yield which can be obtained, its conversion into this same β-chlorcrotonolactone by heating with acids seemed to us of sufficient importance to warrant an experiment in this direction. We therefore heated to boiling 0.7 grm. of the acid with 7 grm. of sulphuric acid of sp. gr. 1.43. Carbonic dioxide was slowly evolved, and the sulphuric acid became strongly colored. After boiling for several hours the solution was cooled, diluted, and extracted with ether. The ethereal extract was then washed with a dilute solution of sodic carbonate, which took up a small amount of the unaltered dichlorpyromucic acid, and dried with calcic chloride. The greater part of the ether

was removed by distillation, the residue transferred to a weighing tube and heated to 60–80° *in vacuo*. The liquid residue which remained weighed 0.13 grm., and on cooling to 13° it almost completely solidified. The well pressed crystalline solid remained friable at the temperature of the room (20°) and melted at 25–26°. Recrystallization from a mixture of ether and ligroin failed to raise this melting point. It was thus proved that the β-chlorcrotonolactone had been formed by the decomposition of the βδ-dichlorpyromucic acid.

a-CHLORCROTONOLACTONE.

The a-chlorcrotonolactone melting at 52–53° was prepared several years ago by Hill and L. L. Jackson * through the decomposition of the γδ(χ)-dichlorpyromucic acid. The close relationship between this substance and a body of similar composition containing bromine, which had been discovered by Hill and Sanger,† was recognized at the time, but no attempt was made to establish experimentally this connection. The body containing bromine, which was described by Hill and Sanger, has already been shown to be the a-bromcrotonolactone, and it is easy to establish the identity in structure of the bromine and chlorine derivatives through the reaction with aniline. The a-chlorcrotonolactone when dissolved in dilute alcohol yields with aniline the a-phenylamidocrotonolactone melting at 217–218°, which we have already described as prepared in the same way from the a-bromcrotonolactone.

Since the a-bromcrotonolactone had been made from the βδ-dibrompyromucic acid through the reduction of the brommaleylbromide, which is formed from it by the action of bromine, it seemed to us of interest to prepare the a-chlorcrotonolactone by the same method from the βδ-dichlorpyromucic acid. Pure βδ-dichlorpyromucic acid was suspended in 25 times its weight of cold water, and dissolved by the cautious addition of sodic carbonate. Two molecules of bromine were then added to the feebly alkaline solution, and the whole allowed to stand over night. As the oil which had separated would not crystallize when strongly cooled and scratched, it was taken up with ether, and the residue left on the evaporation of the ether dissolved in 80 per cent acetic acid. Zinc dust was then added to this solution with careful cooling. When the reaction appeared to be complete, the filtered solution was diluted, extracted with ether, the ethereal solution washed with sodic carbonate and distilled. The

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* These Proceedings, XXIV. 353.   † Ibid., XXI. 158.

residue soon crystallized in long slender prisms, which when recrys-
tallized from ligroin melted at 52–53°, and in other respects showed
the behavior of the a-chlorcrotonolactone. The βδ-dichlorpyromucic
acid, like the corresponding acid containing bromine, may, therefore,
be made to yield either the a- or the β-chlorcrotonolactone. While
we had no doubt that the γδ-dichlorpyromucic acid would show an
essentially different behavior, and would yield, when treated in this
way, the same a-chlorcrotonolactone which it gives when heated with
acids, we thought it worth while to establish the fact by experiment.
The γδ-dichlorpyromucic acid was therefore treated with bromine in
a feebly alkaline solution, and the oil, which was thus formed, was
then reduced with zinc dust and glacial acetic acid. It was easy to
isolate, as before, the a-chlorcrotonolactone melting at 52–53° with its
characteristic properties.

a-PHENOXY-β-BROMCROTONOLACTONE.

Many years ago Hill and Stevens [*] prepared from mucobromic
acid, by the action of potassic phenylate, a derivative of mucobromic
acid, in which one atom of bromine was replaced by the phenoxy
group, and to which they gave the name mucophenoxybromic acid.[†]
They showed that this acid had the same general structure as the
mucobromic acid, in that it could be converted by oxidation into a
phenoxybrommaleic acid, and that it yielded on decomposition with
alkalies a phenoxybromacrylic acid. The stability of the latter acid
in alkaline solution led them to the conclusion that it contained the
phenoxy group in the a position. Although none of the substituted
crotonolactones which we had studied could directly be converted into
the salts of the oxy-acids, it seemed to us probable that the corre-
sponding bodies containing the phenoxy group would react more
smoothly. As the preliminary experiments which we made on the
action of sodic or potassic phenylate upon the dibromcrotonolactone
gave us little hope that the desired bodies could be made in this way,
we turned to the mucophenoxybromic acid, and found that the a-phe-

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[*] These Proceedings, XIX. 262.

[†] Beilstein in the second edition of his " Handbuch der organischen Chemie "
(II. 429) has seen fit to change this name to phenoxymucobromic acid. It is
quite possible that we might have selected a better name for our new body, but
it certainly would be difficult to find one more misleading than that which
Beilstein has chosen to give it. Whatever else it may be, it certainly is *not* a
phenoxymucobromic acid.   H. B. H.

noxy-β-bromcrotonolactone could easily be made by the reduction of its bromanhydride.

The mucophenoxybromylbromide was not described by Hill and Stevens, but we found that it could be made without difficulty, in nearly theoretical quantity, by the action of phosphorous tribromide. We used but little more than one molecule of the tribromide to three molecules of the acid, and heated at 100°. When the liquid product became turbid with the separation of phosphorous acid, we added cold water with constant shaking. The bromide immediately separated in a granular form, and could be recrystallized from small quantities of alcohol. It formed fine concentrically grouped needles, which melted at 95–96°.

0.2363 grm. substance gave 0.2656 grm. AgBr.

	Calculated for $C_4H(OC_6H_5)Br_2O_2$	Found.
Br	47.90	47.82

Mucophenoxybromylbromide is readily soluble in ether, chloroform, or benzol, readily soluble in hot alcohol, more sparingly in cold, and sparingly soluble in ligroin. With alkalies in alcoholic solution it gives a yellow color. The reduction of this body to the corresponding lactone is slowly but completely effected by stannous chloride and hydrochloric acid at ordinary temperatures, if a little alcohol be added at the same time to facilitate solution. We have found it more convenient, however, to use zinc dust and acetic acid. Since the lactone is almost insoluble in dilute acetic acid, and an excess of zinc dust apparently does no harm, we suspended the bromide in twice its weight of glacial acetic acid (99.5 per cent), and slowly added with careful cooling an excess of zinc dust. After standing for several hours, the reduction is complete, and the addition of water to the filtered solution throws down a beautifully crystalline substance, which may be recrystallized from alcohol. The product thus obtained proved on analysis to have the composition of a phenoxybromcrotonolactone. The weight of the lactone as precipitated by water was 80 per cent of the theoretical amount.

I. 0.3929 grm. substance gave 0.6796 grm. CO_2 and 0.1008 grm. H_2O.
II. 0.1906 grm. substance gave 0.1410 grm. AgBr.

	Calculated for $C_4H_2(OC_6H_5)BrO_2$.	Found. I.	II.
C	47.07	47.18	
H	2.75	2.85	
Br	31.37		31.48

The *a*-phenoxy-*β*-bromcrotonolactone is readily soluble in ether, chloroform, benzol, glacial acetic acid, or in hot alcohol, and but sparingly soluble in cold alcohol, or in ligroin. It crystallizes in six-sided plates which melt at 72°. It dissolves slightly in boiling water, and volatilizes slowly with steam. In alcoholic solution it is not attacked by aniline at ordinary temperatures. With aqueous alkalies it is slowly carried into solution, on heating, with the formation of the corresponding salts of the oxy-acid.

a-Phenoxy-β-brom-γ-oxycrotonic Acid. If the *a*-phenoxy-*β*-bromcrotonolactone is dissolved in a hot solution of potassic hydrate, and after thorough cooling a slight excess of hydrochloric acid is added, the solution soon becomes filled with colorless pearly scales of the phenoxybromoxycrotonic acid. For analysis the substance was merely washed well with cold water, and dried over sulphuric acid.

I. 0.2782 grm. substance gave 0.4484 grm. CO_2 and 0.0857 grm. H_2O.

II. 0.1588 grm. substance gave 0.1092 grm. AgBr.

	Calculated for $C_4H_4(OC_6H_5)BrO_3$.	Found. I.	II.
C	43.95	43.96	
H	3.30	3.08	
Br	29.30		29.25

The *a*-phenoxy-*β*-brom-γ-oxycrotonic acid is readily soluble in alcohol or ether, quite readily soluble in hot chloroform or benzol, and almost insoluble in ligroin. From chloroform it crystallizes in brilliant flat rectangularly terminated prisms. It is very sparingly soluble in cold water, and when warmed it dissolves somewhat more freely, but the solution immediately grows turbid with the formation of the still more sparingly soluble lactone. The identity of the phenoxybromcrotonolactone formed in this way was established by analysis.

0.2696 grm. substance gave 0.2007 grm. AgBr.

	Calculated for $C_4H_2(OC_6H_5)BrO_2$.	Found.
Br	31.37	31.66

The melting point of the acid cannot be determined with precision, since it is converted into the lactone by heat, but under ordinary conditions it is found to be about 98°. The loss of weight which we observed on melting the acid by short exposure to a temperature of 110°, and allowing the fused mass to stand over sulphuric acid, corresponded to a little more than one molecule of water.

0.6318 grm. substance lost 0.0450 grm. H_2O.

	Calculated for $C_4H_4(OC_6H_5)BrO_3$.	Found.
H_2O	6.59	7.12

Baric a-phenoxy-β-brom-γ-oxycrotonate, $Ba(C_4H_3(OC_6H_5)BrO_3)_2$. $3 H_2O$. — The barium salt is readily soluble even in cold water, and crystallizes in flat prisms with rectangular terminations. It apparently contains three molecules of water, almost the whole of which it readily loses over sulphuric acid.

0.5891 grm. air-dried salt lost over sulphuric acid 0.0430 grm. H_2O, and at 100° it lost 0.0052 grm. H_2O in addition.

	Calculated for $Ba(C_4H_3(OC_6H_5)BrO_3)_2$. $3 H_2O$.	Found.
H_2O	7.35	8.18

0.4939 grm. anhydrous salt gave 0.1677 grm. $BaSO_4$.

	Calculated for $Ba(C_4H_3(OC_6H_5)BrO_3)_2$.	Found.
Ba	20.11	19.97

The anhydrous salt dissolves without difficulty in strong alcohol, but in a few moments the solution turns solid with the separation of finely felted needles of a salt containing alcohol of crystallization. The same salt may also be obtained by dissolving the hydrous salt in hot alcohol. We have been unable to obtain satisfactory determinations of the amount of alcohol which is thus taken up, since the salt effloresces very rapidly on exposure to the air, and loses the last part of its alcohol with great difficulty.

a-PHENOXY-β-CHLORCROTONOLACTONE.

It seemed to us desirable to confirm the results which we had obtained with the phenoxybromcrotonolactone by preparing also the corresponding bodies containing chlorine. 'Hill and Stevens had made no experiments as to the action of potassic phenylate upon mucochloric acid, but we found that mucophenoxychloric acid could readily be made in this way. As we were interested only in the preparation of the phenoxychlorcrotonolactone, Mr. H. P. Nash undertook a more careful study of this acid, and will present his results in a separate paper. From the mucophenoxychloric acid we prepared without difficulty the corresponding bromanhydride by the action of phosphorous tribromide. The reaction ran smoothly, and gave us, as in the previous cases, which we have described more in detail, about 90 per cent of the theoretical yield. The body was readily soluble in ether, chloroform, benzol, or glacial acetic acid. It was very readily soluble

in hot alcohol, more sparingly in cold, very sparingly soluble in cold ligroin, though more easily soluble in hot. When recrystallized from small quantities of alcohol or from ligroin, it was obtained in radiating needles which melted at 89–90°.

0.2320 grm. substance gave 0.2631 grm. AgCl + AgBr.

	Calculated for $C_4H(OC_6H_5)ClO_2Br$.	Found.
Cl + Br	39.89	39.53

In the reduction of the mucophenoxychlorylbromide to the corresponding lactone we followed the method which had already proved convenient with the mucophenoxybromylbromide. Zinc dust was slowly added with careful cooling to the bromide dissolved in glacial acetic acid. When the reduction was complete, the filtered solution was diluted with water, and the crystalline body which was thus thrown down was recrystallized from a small amount of alcohol. The lactone which was precipitated by water amounted to 76 per cent of the theoretical yield.

I. 0.3243 grm. substance gave 0.6765 grm. CO_2 and 0.0995 grm. H_2O.
II. 0.2256 grm. substance gave 0.1541 grm. AgCl.

	Calculated for $C_4H_2(OC_6H_5)ClO_2$.	Found. I.	II.
C	57.02	56.89	
H	3.33	3.40	
Cl	16.87		16.89

The a-phenoxy-β-chlorcrotonolactone is readily soluble in ether, chloroform, benzol, carbonic disulphide, and in hot alcohol or ligroin, although but sparingly soluble in these solvents when cold, and almost insoluble in water. From alcohol it crystallizes in six-sided plates, or flattened prisms, which melt at 67–68°. In alcoholic solution it is not affected by aniline at ordinary temperatures. When heated with aqueous alkalies it is gradually carried into solution with the formation of the salt of the corresponding oxy-acid.

a-Phenoxy-β-chlor-γ-oxycrotonic Acid, $C_4H_4(OC_6H_5)ClO_3$. — If the a-phenoxy-β-chlorcrotonolactone is dissolved in a moderately dilute solution of potassic hydrate by the aid of heat, and to the well cooled solution a slight excess of hydrochloric acid is added, the phenoxychloroxycrotonic acid separates almost immediately in colorless pearly scales. The crystals were removed by filtration, thoroughly washed with cold water and dried over sulphuric acid. The substance was then analyzed without further purification.

I. 0.4291 grm. substance gave 0.8242 grm. CO_2 and 0.1541 grm. H_2O.
II. 0.2160 grm. substance gave 0.1342 grm. AgCl.

	Calculated for $C_4H_4(OC_6H_5)ClO_3$.	Found. I.	II.
C	52.51	52.37	
H	3.94	3.99	
Cl	15.52		15.36

a-Phenoxy-β-chlor-γ-oxycrotonic acid crystallizes in flat rectangularly truncated prisms which melt at about 76°, but the melting point varies with the rapidity of the heating. It is very soluble in alcohol or ether, quite readily soluble in chloroform or benzol, less soluble in carbonic disulphide or ligroin, and sparingly soluble in water. On heating with water it behaves like the compound containing bromine, which has already been described, and is rapidly converted into the lactone. This conversion is immediately effected when the acid is heated to its melting point. The acid was melted by short exposure to a temperature of 110°, and the fused mass thoroughly dried over sulphuric acid. The loss in weight corresponded almost exactly to that required by one molecule of water.

0.4068 grm. substance lost 0.0333 grm. H_2O.

	Calculated for $C_4H_4(OC_6H_5)ClO_3$.	Found.
H_2O	7.88	8.11

The acid may also be converted into the lactone by longer continued heating at a temperature below its melting point, and this change seems to take place slowly even at ordinary temperatures. After the lapse of many weeks a combustion of the material which had previously given us the proper percentage of chlorine showed that the acid had in part been converted into the lactone.

0.2004 grm. substance gave 0.4018 grm. CO_2 and 0.0676 grm. H_2O.

	Calculated for $C_4H_4(OC_6H_5)ClO_3$.	Calculated for $C_4H_2(OC_6H_5)ClO_2$.	Found.
C	52.51	57.02	54.69
H	3.94	3.33	3.75

Baric a-phenoxy-β-chlor-γ-oxycrotonate, $Ba(C_4H_3(OC_6H_5)ClO_3)_2$. 3 H_2O. — The barium salt of the acid is very soluble even in cold water, and crystallizes in long colorless prisms. The air-dried salt contains three molecules of water, all of which it loses over sulphuric acid.

0.5906 grm. air-dried salt lost over sulphuric acid 0.0492 grm. H_2O,
and when heated at 100° it lost in addition 0.0002 grm. H_2O.

	Calculated for $Ba(C_4H_3(OC_6H_5)ClO_3)_2 . 3 H_2O$.	Found.
H_2O	8.36	8.36

0.4814 grm. anhydrous salt gave 0.1869 $BaSO_4$.

	Calculated for $Ba(C_4H_3(OC_6H_5)ClO_3)_2$.	Found.
Ba	23.19	22.82

This salt behaves toward alcohol precisely like the baric phenoxy-bromoxycrotonate, and forms the same finely felted needles.

MUCOBROMIC ACID.

It was shown many years ago by Hill and O. R. Jackson,[*] that mucobromic acid could be converted into dibrommaleic acid by oxidation with argentic oxide. When their investigation was completed (1880), it was already known that phenylhydrazine reacted upon certain aldehydes, but experimental evidence as to the generality of the reaction had not accumulated, and the importance of this body as a reagent for aldehydes and ketones was not urged by E. Fischer [†] until several years later. The characteristic behavior of hydroxylamine with aldehydes and ketones was also not discovered by V. Meyer [‡] until two years later. Since the facts which we have described in the preceding pages, tended to show that mucobromic acid was an oxylactone and not an aldehyde acid, it was evidently necessary for us to study its behavior toward phenylhydrazine and hydroxylamine. Phenylhydrazine has unfortunately given us no bodies the physical properties of which invited further investigation, but with hydroxylamine we have been more successful. We have also studied the action of ammonia upon ethylmucobromate, and found that mucobromamide is thus formed.

Mucobromoxime, $C_4H_3Br_2NO_3$. — Hydroxylamine acts with great ease upon mucobromic acid, but we have been able to isolate the oxime only when the reaction takes place in an alkaline aqueous solution. The decomposition is almost instantaneous, so that after the lapse of a few minutes the solution deposits upon acidification the

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[*] These Proceedings, XVI. 186.

[†] Berichte d. deutsch. chem. Gesellsch., XVII. 572.

[‡] Ibid., XV. 1165, 1324, 1527, 2778, 2783; XVI. 822.

oxime in a granular condition. This granular precipitate was at once removed by filtration, well washed with cold water, and dried over sulphuric acid.

I. 0.2397 grm. substance gave 0.1575 grm. CO_2 and 0.0415 grm. H_2O.
II. 0.3133 grm. substance gave 0.2043 grm. CO_2.[*]
III. 0.2524 grm. substance gave 0.3481 grm. AgBr.

	Calculated for $C_4H_3Br_2NO_3$.	Found. I.	II.	III.
C	17.58	17.92	17.58	
H	1.10	1.92		
Br	58.61			58.68

This oxime is readily soluble in alcohol or ether, and but sparingly soluble in chloroform or benzol. In cold water it is also sparingly soluble, but dissolves readily on boiling. If the hot solution is immediately cooled the oxime anhydride separates, but otherwise the acid ammonium salt of dibrommaleic acid is formed, and remains in solution. The oxime has no definite melting point, but is evidently converted into the anhydride by heat. It usually melts, at least in part, at about 90°, but this point varies with the rate of heating.

Mucobromoxime Anhydride, $C_4HBr_2NO_2$. — Under ordinary conditions the only product formed by the action of hydroxylamine or its hydrochlorate upon mucobromic acid is the anhydride of the oxime. Moreover, if in the preparation of the oxime by the method just described the precipitated substance is allowed to stand for several hours in the mother liquor, the anhydride is formed. The material used in Analysis III. was made by the action of hydroxylamine hydrochlorate upon a solution of mucobromic acid in strong methyl alcohol; for the other determinations, preparations were employed which had been made in a solution in dilute methyl alcohol with the addition of one equivalent of sodic carbonate. In each case the reaction ran rapidly at ordinary temperatures, and the anhydride which separated was washed well with cold water, and dried over sulphuric acid.

I. 0.2927 grm. substance gave 0.4334 grm. AgBr.
II. 0.2393 grm. substance gave 0.3547 grm. AgBr.
III. 0.1801 grm. substance gave 0.2670 grm. AgBr.
IV. 0.2014 grm. substance gave 10.0 c.c. of moist nitrogen at 19° and under a pressure of 753 mm.
V. 0.3127 grm. substance gave 14.5 c.c. of moist nitrogen at 15° and under a pressure of 764 mm.

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* The hydrogen in this combustion was lost.

	Calculated for $C_4HBr_2NO_2$.	I.	II.	Found. III.	IV.	V.
Br	62.75	63.00	63.07	63.08		
N	5.49				5.65	5.45

Mucobromoxime anhydride dissolves quite readily in alcohol, chloroform, or benzol; with somewhat more difficulty in ether or carbonic disulphide; and is almost insoluble in ligroin. It crystallizes in dendritic needles, which melt at about 117–118°, but this melting point varies with the conditions under which it is taken. If the melted substance be heated to a higher temperature, it solidifies again below 140° and melts then for a second time at 218°. This behavior is due to the conversion of the anhydride into the isomeric dibrommalein-imide, which melts, according to Ciamician and Silber,[*] at 225°. If this isomerization is brought about by plunging the tube containing a considerable quantity of the substance into a bath heated to 115°, the reaction is violent, but also attended with decomposition. The anhydride is sparingly soluble in cold water, although more readily in hot. If the hot solution is quickly cooled the anhydride separates, but on prolonged heating it is completely converted into the acid ammonium salt of dibrommaleic acid. This acid was identified through its characteristic barium salt and the melting point (114°) of its anhydride.

Methyl Ester of Mucobromoxime, $C_4H_2Br_2NO_3CH_3$. — Although hydroxylamine hydrochlorate reacts at ordinary temperatures upon mucobromic acid when dissolved in strong methyl alcohol, and forms the mucobromoxime anhydride, if the reaction takes place at the boiling point of the methyl alcohol the methyl ester of the oxime results. The same body is also formed when the anhydride is boiled for a short time with methyl alcohol. For its preparation we found it advantageous to dissolve mucobromic acid in rather less than twice its weight of methyl alcohol, to add a little more than one molecule of hydroxylamine hydrochlorate dissolved in the smallest possible quantity of water, and to boil with reverse cooler for twenty minutes. On cooling, the methyl ester then separated in abundance.

I. 0.4336 grm. substance gave 0.3370 grm. CO_2 and 0.0915 grm. H_2O.
II. 0.2946 grm. substance gave 0.3899 grm. AgBr.

	Calculated for $C_4H_2Br_2NO_3CH_3$.	Found. I.	II.
C	20.90	21.19	
H	1.74	2.34	
Br	55.75		56.31

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[*] Berichte d. deutsch. chem. Gesellsch., XVII. 556.

The methyl ester of mucobromoxime is readily soluble in alcohol, somewhat more sparingly soluble in ether, and very sparingly soluble in chloroform or benzol. It is also very sparingly soluble in cold water, but dissolves freely on heating, and, if the solution is quickly cooled, it separates in finely felted needles. On continued boiling it is converted into dibrommaleinimide, and the same change is also effected by longer boiling with methyl alcohol. The ester melts at 146–147°, and at a slightly higher temperature solidifies with the formation of dibrommaleinimide, which again melts at 218°. The conversion of the ester into the imide may also be brought about by dissolving it in sodic carbonate, and acidifying the solution with hydrochloric acid. The imide melting at 218° is thus thrown down. If the alkaline hydrates are used to dissolve the ester, great care must be used to avoid an excess. This same ester may also be made by the action of hydroxylamine hydrochlorate upon methyl mucobromate dissolved in methyl alcohol. We found, however, that substantially no reaction took place when a ten per cent solution of the ester stood at ordinary temperatures for several days, either with free hydroxylamine or with its hydrochlorate. The solutions when cooled with ice and salt deposited no crystals in material amount, and on dilution with water the original ester was recovered essentially unchanged. With free hydroxylamine there seemed to be but slow action even on boiling; but on boiling the solution containing the hydrochlorate for half an hour, a copious separation of the methyl ester of the mucobromoxime melting at 146–147° was obtained on cooling. On boiling for a longer time this ester was almost wholly converted into dibrommaleinimide melting at 218°.

Although it had been found that the methyl ester of mucobromoxime could not be dissolved in alkalies without the formation of dibrommaleinimide, it seemed to us possible that we might form a silver salt. On the addition of an alcoholic solution of argentic nitrate to an alcoholic solution of the ester, no salt was precipitated, and no crystals separated on standing. Alcoholic ammonia was then cautiously added, and the first drop brought down a heavy yellow pulverulent precipitate, although the addition of two molecules was necessary to complete the precipitation. The salt was insoluble in water or alcohol, and was not affected by an excess of ammonia. On analysis it proved to be an ammonio-silver salt of dibrommaleinimide, corresponding to the ammonio-silver compound of dichlormaleinimide described by Ciamician and Silber.* Nitric acid decomposed it with the liberation of dibrommaleinimide.

* Berichte d. deutsch. chem. Gesellsch., XVI. 2394.

I.   0.2916 grm. substance gave with HBr 0.1440 grm. AgBr.

II.   0.2384 grm. substance gave with HNO_3 and $AgNO_3$ 0.2347 grm. AgBr.

III.   0.3502 grm. substance gave 22.2 c.c. of moist nitrogen at 19° and under a pressure of 754 mm.

	Calculated for $C_4Br_2NO_2AgNH_3$.	I.	Found. II.	III.
Ag	28.51	28.37		
Br	42.23		41.89	
N	7.39			7.37

A salt which closely resembles that which we have just described is precipitated when an alcoholic solution of argentic nitrate is added to an alcoholic solution of dibrommaleinimide. It can contain no ammonia, however, and is the silver salt of the imide.

0.3153 grm. substance gave 10.7 c.c. of moist nitrogen at 17° and under a pressure of 777 mm.

	Calculated for $C_4Br_2NO_2Ag$	Found.
N	3.87	4.02

The strongly acid filtrate from this salt gave with alcoholic ammonia an ammonio-silver salt identical with that prepared from the methyl ester of mucobromoxime.

0.3553 grm. substance gave 21.9 c.c. of moist nitrogen at 17° and under a pressure of 775 mm.

	Calculated for $C_4Br_2NO_2AgNH_3$.	Found.
N	7.39	7.30

In the preparation of the mucobromoxime methyl ester directly from mucobromic acid, there is also formed an oil, which, although somewhat soluble in water, is precipitated by the addition of water to the methyl-alcoholic mother liquors. We have not obtained it in a condition fit for analysis, but as it is readily decomposed by water with the formation of dibrommaleic acid it is doubtless an acid ester of this acid.

Mucobromamide, $C_4HBr_2O_2NH_2$ — When ammonia gas is passed into a solution of ethyl mucobromate in dry ether, reaction immediately takes place, and mucobromamide separates. This body may also be prepared by the action of alcoholic ammonia upon an alcoholic solution of the ester at ordinary temperatures, but the product so obtained is dark

colored and must be treated with bone-black in acid solution, and re-crystallized from hot water. We have also prepared mucobromamide by the action of ammonia upon mucobromylbromide dissolved in anhydrous ether.

I. 0.3496 grm. substance gave 0.2426 grm. CO_2 and 0.0555 grm. H_2O.

II. 0.3640 grm. substance gave 0.5342 grm. AgBr.

III. 0.2033 grm. substance gave 10.7 c.c. of moist nitrogen at 18°.5, and under a pressure of 769 mm.

	Calculated for $C_4HBrO_2NH_2$	I.	Found. II.	III.
C	18.68	18.92		
H	1.20	1.77		
Br	62.26		62.44	
N	5.45			6.13

Mucobromamide is nearly insoluble in ether, chloroform, or benzol, and is readily soluble in hot, more sparingly in cold alcohol. It dissolves very readily in hot water, and separates almost completely as the solution cools in colorless dendritic needles, which melt with decomposition at about 170°. Slight impurities apparently lower very greatly this point of melting and decomposition. Alkaline hydrates added in excess carry it completely into solution in the cold without the formation of any color, but, if an excess be not added, the solution rapidly turns brown or black. From the colorless solution the immediate addition of acid reprecipitates the amide unchanged. It may be recrystallized from hot concentrated hydrochloric acid, or from dilute sulphuric acid, but after long heating with concentrated hydrochloric acid, or boiling for a shorter time with distillable hydrobromic acid, mucobromic acid melting at 120° is formed. The amide dissolved readily in fuming nitric acid, and on long standing this solution deposited well formed crystals of dibrommaleinimide melting at 218°. Dilute solutions of chromic acid with an excess of sulphuric acid effected little change even on long boiling, but in concentrated solution oxidation took place and dibrommaleinimide was formed. This same body was also formed when the amide was heated with dry bromine at 100°.

We made many attempts to make from the mucobromamide by the action of hydroxylamine, phenylhydrazine, or aniline, the corresponding derivatives, but in no case were we successful. Either the amide was recovered unchanged, or in a few cases in working with the free bases at higher temperatures a deeper decomposition ensued.

MUCOCHLORIC ACID.

Toward hydroxylamine mucochloric acid behaves in essentially the same way as mucobromic acid, although we have been unable as yet to prepare the anhydride of the oxime, the body which was most readily formed from mucobromic acid. The methyl ester of muco-chloric acid when treated with ammonia gave mucochloramide without difficulty.

Mucochloroxime, $C_4H_3Cl_2NO_3 . \frac{1}{2}H_2O$. — Mucochloric acid was dissolved in a small amount of methyl alcohol, and one equivalent each of hydroxylamine and sodic carbonate dissolved in a little water were added. After the lapse of a few minutes the solution was acidified with hydrochloric acid and the oxime immediately separated. Analyses of the air-dried material (III.) or of the substance dried over sulphuric acid (I. and II.) showed that in each case one half-molecule of water was retained. Since dichlormaleinimide was quickly formed at temperatures below 100°, no attempt was made to dehydrate the substance by heat.

I. 0.2220 grm. substance gave 0.2014 grm. CO_2 and 0.0471 grm. H_2O.

II. 0.2008 grm. substance gave 0.2992 grm. AgCl.

III. 0.1927 grm. substance gave 0.2851 grm. AgCl.

	Calculated for $C_4H_3Cl_2NO_3 . \frac{1}{2}H_2O$.	I.	Found. II.	III.
C	24.87	24.79		
H	2.07	2.36		
Cl	36.79		36.58	36.85

Mucochloroxime crystallizes in slender felted needles, which are readily soluble in alcohol or ether, and but sparingly soluble in cold water. It dissolves readily in hot water, and if the solution is quickly cooled, it separates apparently unchanged, but on heating for a short time with water it is converted into the acid ammonium salt of dichlormaleic acid. The identity of the acid extracted by ether from the acidified solution was established by the melting point of its anhydride (119°). The melting point of the oxime cannot be determined with precision, but it lies in the neighborhood of 90°. The melted oxime passes into the dichlormaleinimide which solidifies and again melts at 175–177°.

Methylester of Mucochloroxime, $C_4H_2Cl_2NO_3CH_3$. — The methyl ester of mucochloroxime is formed when a cold solution of the oxime

in methyl alcohol is allowed to stand for twenty-four hours, or when mucochloric acid is dissolved in its own weight of methyl alcohol, hydroxylamine hydrochlorate dissolved in a little water added in some-what more than equivalent quantity, and the whole allowed to stand at ordinary temperatures. If the solution is boiled even for a short time the chief product is dichlormaleinimide. The ester may also be made by the action of hydroxylamine hydrochlorate upon methyl mucochlo-rate, provided the solution in methyl alcohol be allowed to stand for several days.

0.1676 grm. substance gave 0.2437 grm. AgCl.

	Calculated for $C_4H_2Cl_2NO_3CH_3$.	Found.
Cl	35.86	35.94

The methyl ester of the mucochloroxime crystallizes in flattened needles, the melting point of which varies with the mode of heating. When introduced into a heated bath the substance melts promptly when the temperature is held at 135°. At higher temperatures the melted ester again solidifies, with the formation of dichlormaleinimide, which in its turn melts at 173–174°. The ester is readily soluble in alcohol, ether, or chloroform, and but sparingly soluble in benzol or carbonic disulphide. It is also sparingly soluble in cold water, but dissolves more readily in hot water, and, if the solution is quickly cooled, it separates in long felted needles. On longer heating with water it is converted into dichlormaleinimide. The ester may also be converted into the imide by dissolving it in a solution of sodic carbonate, and acidifying with hydrochloric acid, provided the solution is cold, and moderately concentrated, and the acid is immediately added.

Mucochloramide, $C_4HCl_2O_2NH_2$. — Mucochloramide is readily formed when ammonia gas is passed into a solution of methyl muco-chlorate in dry ether. The hard dark-colored mass which separates is ground up in a mortar with small quantities of cold water. The greater part of the coloring matter is thus removed, and the residue may then be recrystallized from boiling water.

0.2115 grm. substance gave 0.3606 grm. AgCl.

	Calculated for $C_4HCl_2O_2NH_2$	Found.
Cl	42.27	42.15

Mucochloramide is readily soluble in alcohol, sparingly soluble in ether, and almost insoluble in chloroform. It dissolves readily in hot water, and as the solution cools the greater part is deposited in the

form of small oblique prisms, which melt at about 166°. Like muco-
bromamide it dissolves readily in solutions of the alkaline hydrates,
and is reprecipitated unchanged if the alkaline solution is immediately
acidified. On boiling for some time with concentrated hydrochloric
acid, it is converted into mucochloric acid, as was shown by the melt-
ing point, 124°.

MUCOPHENOXYBROMIC ACID.

Mucophenoxybromoxime, $C_4H_3(OC_6H_5)BrNO_3$. — We have found
that hydroxylamine readily reacts upon mucophenoxybromic acid,
and that the corresponding oxime is formed both in alkaline and acid
solution. It may conveniently be prepared by adding to a solution of
the acid in 20 times its weight of 50 per cent methyl alcohol the
equivalent amount of hydroxylamine hydrochlorate. After standing
for a short time at ordinary temperatures the oxime begins to sepa-
rate in beautiful clusters of long needles, and in a few hours the
reaction is completed.

0.2717 grm. substance gave 0.1791 grm. AgBr.

	Calculated for $C_4H_3(OC_6H_5)BrNO_3$.	Found.
Br	27.97	28.04

Mucophenoxybromoxime is readily soluble in alcohol or ether, and
insoluble in chloroform or benzol. It is almost insoluble in cold
water, dissolves but sparingly in boiling, and separates apparently
unchanged if the solution is quickly cooled. On long boiling it is
decomposed, and the solution then contains ammonia and phenoxy-
brommaleic acid. The solution was acidified with hydrochloric acid,
extracted with ether, and the acid removed from the ethereal solution
with sodic carbonate. The alkaline solution then gave on acidification
small clustered needles, which melted at 104–105° when rapidly
heated. On sublimation a crystalline body was obtained which melted
at 91°. According to Hill and Stevens, phenoxybrommaleic acid,
when quickly heated, melts at 104–105°, and we found that their
acid when sublimed yielded the anhydride melting at 91°. The oxime
shows great variation in melting point (120–135°), according to the
mode of heating, and we have not yet been able to show that it is
converted into the phenoxybrommaleinimide by heat. The melted
body did not solidify on further heating, nor did it crystallize on
cooling.

MUCOPHENOXYCHLORIC ACID. [1]

Mucophenoxychloroxime, $C_4H_3(OC_6H_5)ClNO_3$. — This body is formed by the action of either hydroxylamine, or its hydrochlorate, at ordinary temperatures upon mucophenoxychloric acid.   As in previous cases we used diluted methyl alcohol as a solvent.   The oxime began to crystallize almost immediately, and the separation was in a short time complete.   The material used in Analysis I. was prepared by the action of the free base; that in Analysis II. with the hydrochlorate.

I. 0.2025 grm. substance gave 0.1202 grm. AgCl.
II. 0.2137 grm. substance gave 0.1294 grm. AgCl.

	Calculated for $C_4H_3(OC_6H_5)ClNO_3$.	Found.	
		I.	II.
Cl	14.70	14.68	14.97

Mucophenoxychloroxime crystallizes in clustered needles, which melt at 112–125°, according to the mode of heating.   It dissolves readily in alcohol or ether, but is insoluble in chloroform or benzol. It is almost insoluble in cold water, dissolves somewhat more freely on heating, and crystallizes out unchanged if the solution is quickly cooled.   On longer boiling it is decomposed, and the solution then contains the acid ammonium salt of an acid which we have not yet further examined.